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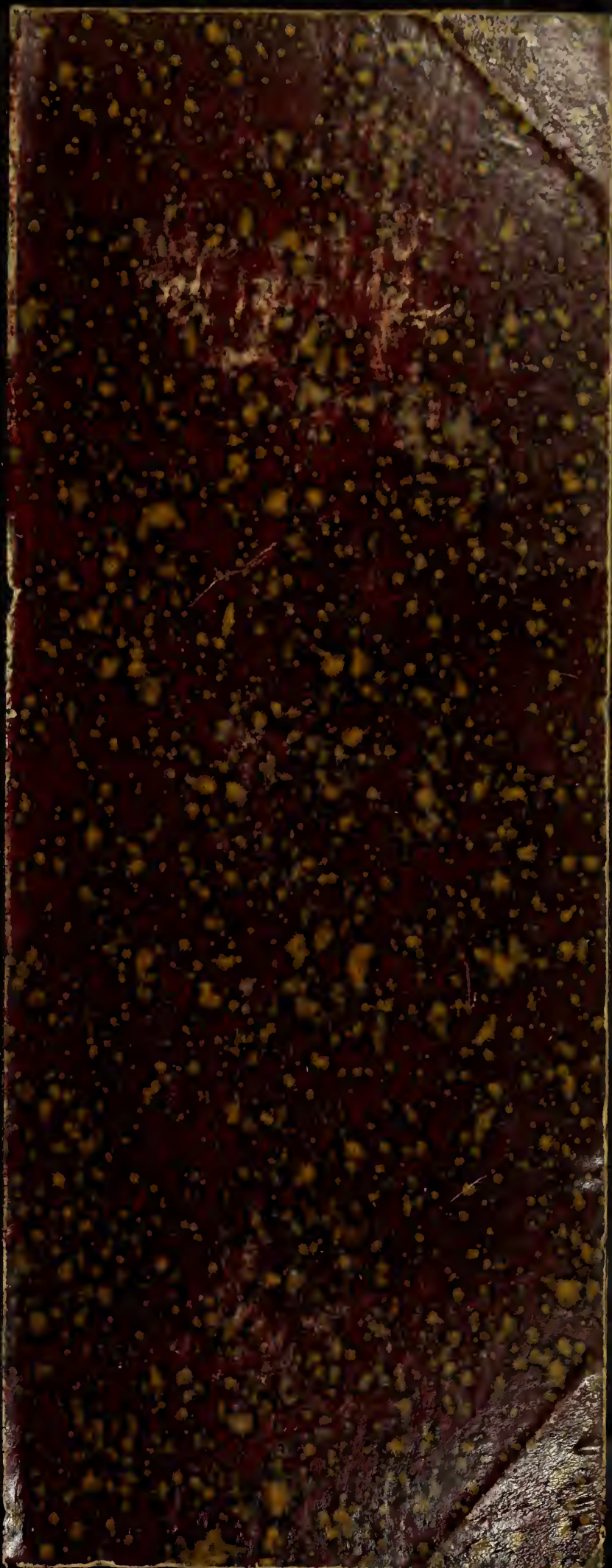
The Influence of some  
Electrolytes upon Clay

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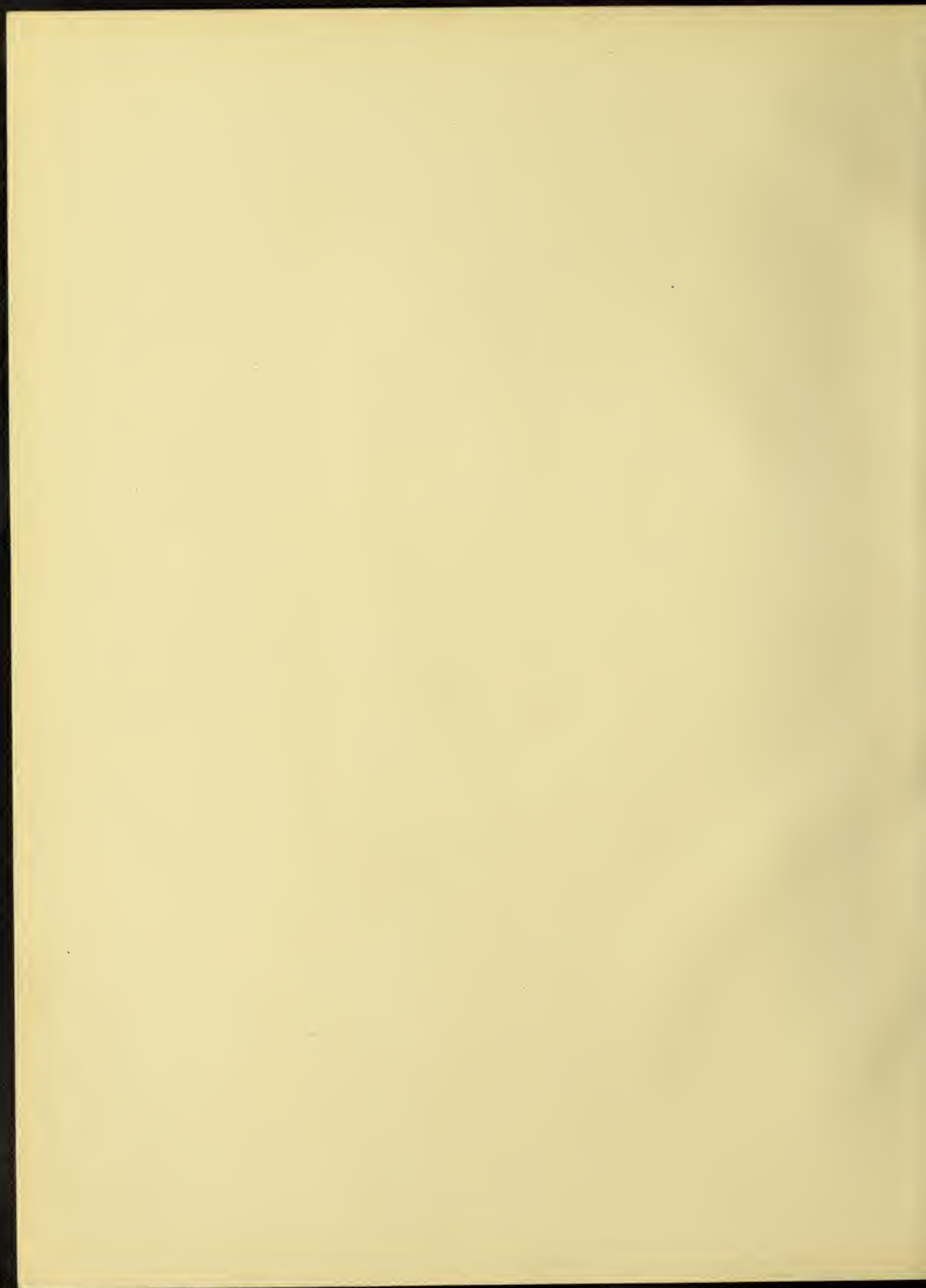


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THE INFLUENCE OF SOME ELECTROLYTES  
UPON CLAY

BY

ROBERT BACK

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THESIS

FOR THE

DEGREE OF BACHELOR OF SCIENCE

IN

CERAMIC ENGINEERING

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COLLEGE OF SCIENCE

UNIVERSITY OF ILLINOIS

1913



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May 31st 1913

THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

Robert Back

ENTITLED The Influence of Some Electrolytes  
Upon Clay.

IS APPROVED BY ME AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

DEGREE OF Bachelor of Science

in Ceramic Engineering

A. V. Bleiringer

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247339





# THE INFLUENCE OF SOME ELECTROLYTES UPON CLAY.

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## The Influence of Some Electrolytes Upon Clay.

### I. Introduction.

#### "Some Views on Colloids and Plasticity."

The work represented by the contents of this bulletin was carried on for the purpose of studying the effects of very small concentrations of electrolytes in solution upon samples of commercial clays, and correlating, if possible, such phenomena with facts known in connection with colloids and disperse systems.

#### Definitions and Theory.

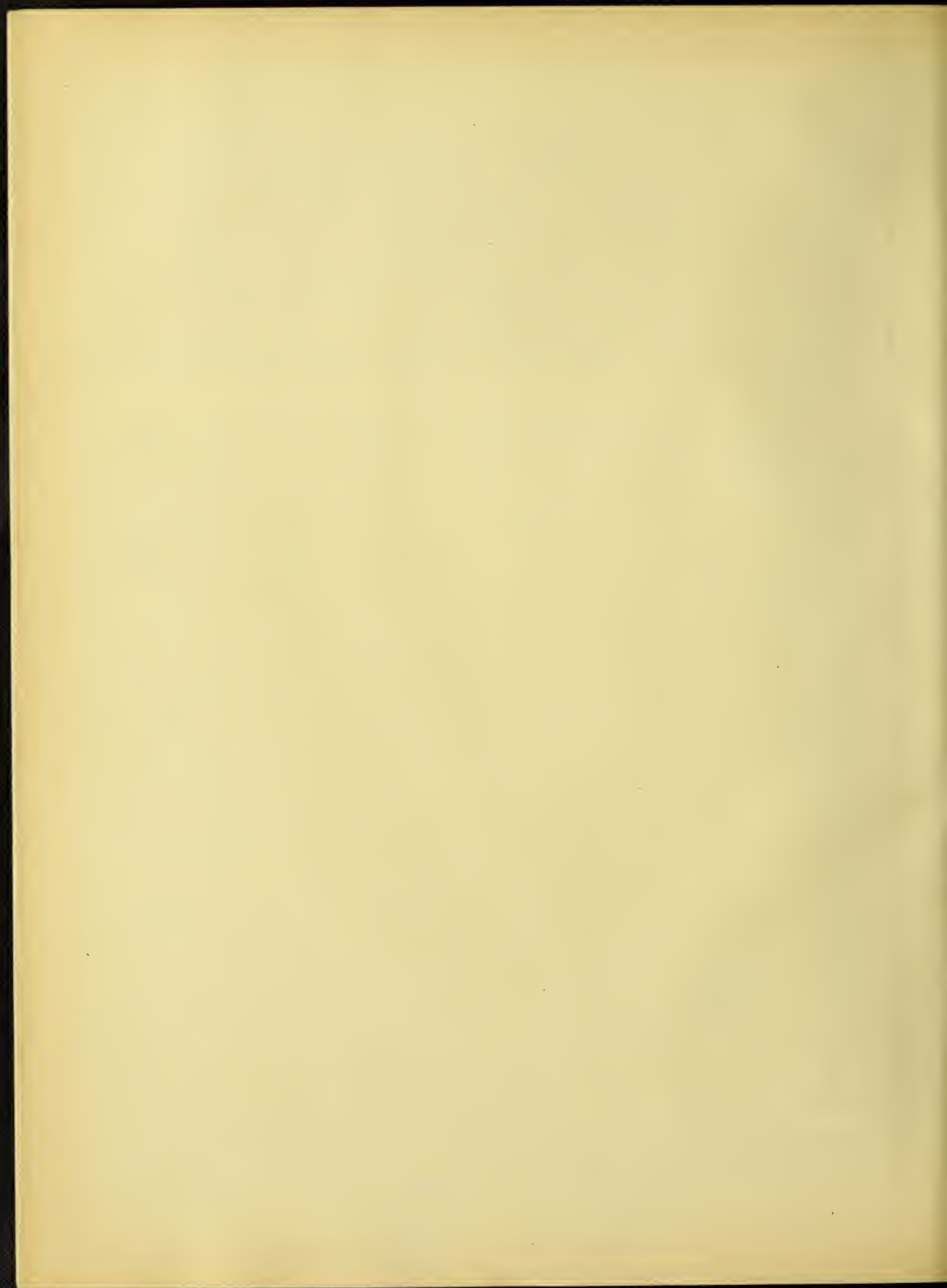
"Clay" is a decomposition product of feldspathic igneous rock, and "commercial clay" is this product or mixtures of such products which have had varying quantities of foreign materials, organic and inorganic, added to them or affecting physical and chemical changes in them. The clays as used in manufacture, then, consist principally of substances whose compositions compare closely to that of the "clay base" or mineral kaolinite,  $(\text{Al}_2\text{O}_3 \cdot 2 \text{SiO}_2 \cdot 2\text{H}_2\text{O})$  admixed with other silicates of aluminium, iron, alkalies, and alkaline earths, as well as residual organic substances and absorbed soluble and insoluble salts. The primary clays are the more simple mixtures, while the secondary or transported and redeposited clays are more complex. Starting with a specific igneous rock which is disintegrating into mineral mixtures which will result in the formation of a clay when due time has elapsed, we may say that the physical structure and behavior and the chemical constitution of the mix is ever varying. The crystalline granular combinations are being broken up and dissociated into grains of varying degrees of

1875  
1876  
1877



fineness until solution and other dissociating forces cause further physical and chemical changes. Finally a quantity of excessively fine grains is produced which are so small that they show varying amplitudes of Brownian movement. By virtue of their small size they are acted upon by water and become completely changed as regards structure. They lose their integrity by the taking up of water and assume the character of a large class of materials commonly called colloidal.

Clay Colloids:- Investigators who are interested in the study of clays seem to have different conceptions of just what clay minerals in the colloidal state are. All agree that very fine dispersion of matter is essential to the colloid state, but difference of opinion arises when considering the rôle which water plays when in contact with these minute particles. Some argue that the clay colloid is the clay mineral substance in the limiting degree of fineness of grain which is tenaciously holding films of water about its grains by virtue of purely physical forces such as adhesion forces. Then they proceed to attribute many of the physical properties of clays to this association of water and clay particles without considering the chemical aspect of the subject which, in addition to agreeing with nearly all the physical aspects of colloidal solution, would go further and align many phenomena known in the field of colloidal chemistry with those in molecular chemistry and thereby support such theories of the latter in regard to "solution", "crystallization," "ionic dissociation of molecules," etc. Other scientists believe that, in the clay colloid, water is absorbed or combined with the mineral particles. The electrolytic dissociation theory comes to our aid in studying clay colloids. When we recall



that no matter is totally insoluble we can conceive of pseudo-solutions of minerals due to dispersion of molecular aggregates under the influence of different solvents. Such a suspension of electrically charged colloid particles approaching molecular dimensions would give us what we call "colloid sols." The discharged coagulated particles forming complex groups and eventually visible and deposited substance form what we call "colloid gels."

In the light of this reasoning we can understand electrification phenomena for example, and the reason for colloid particles appearing as anisotropic<sup>1</sup> bodies may lie in the fact that the different minerals of clay form physical aggregates susceptible to the action of electrolytes and responding to differences in potential. It may be with colloids as with the ions of dissolved substances. Indeed, P. P. Von Weimarn<sup>2</sup> has presented a "Crystalline Theory on the Nature of the Colloidal State" which is evoking great interest at the present time.

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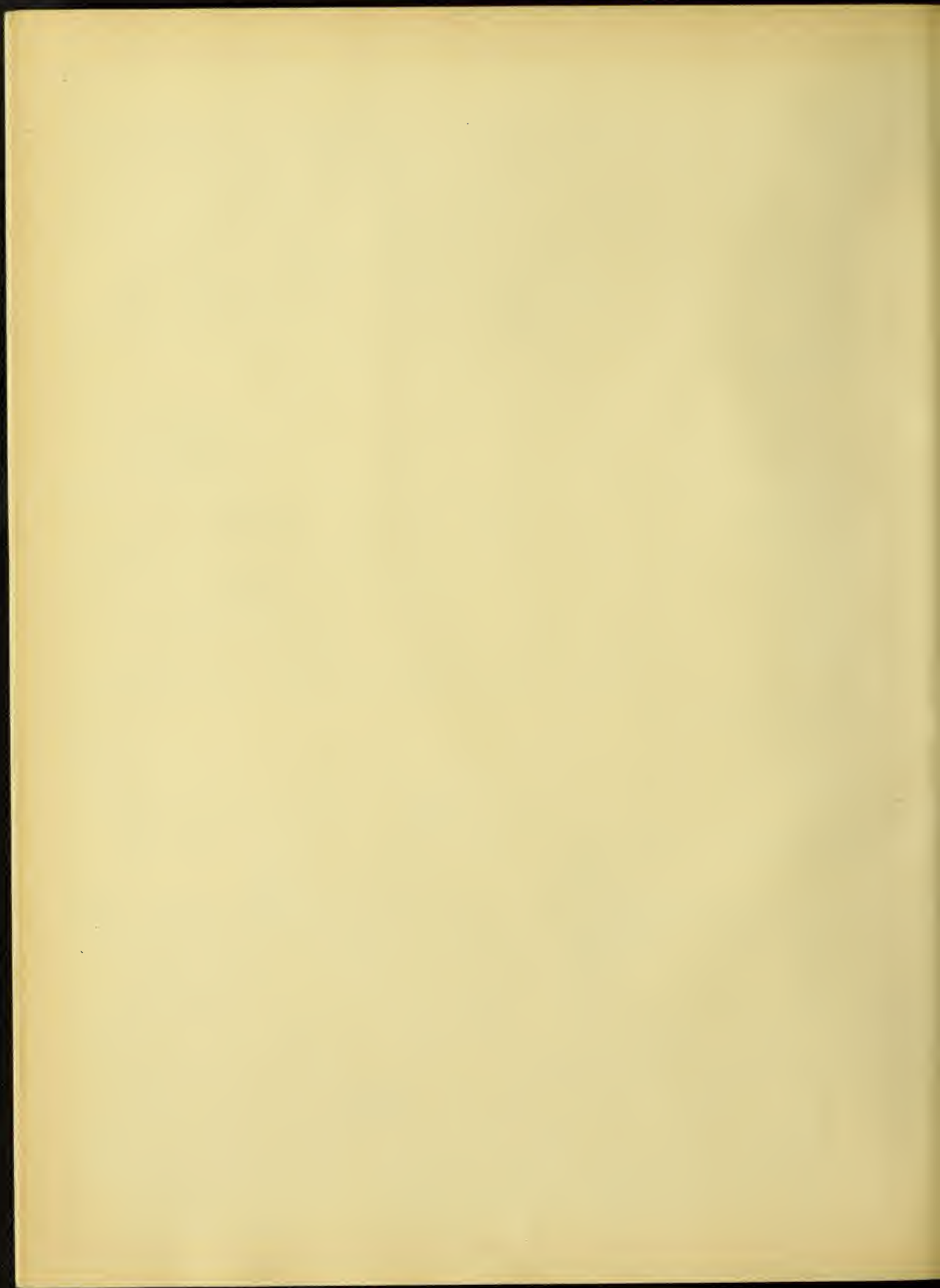
1. E. F. Burton - "On The Physical Aspect of Colloidal Solutions."
2. V. Pöschl, p. 95, Compare Koll. Zeitschr, ii., 81 (1907) and works in other volumes.

#### Summary of V. Weimarn's Theory.

"This Theory is a special form of the suspension theory which deals more completely with the forms of the disperse phase. The particles of colloidal solutions are crystalline. The crystalline state is the only possibility of matter. Accordingly, gases, liquids, and solids are crystalline. P. P. Von Weimarn puts forward the following data in support of the assumption that the disperse phase is crystalline-

For the formation of a precipitate solutions having a definite concentration must be employed. During the course of several experiments it was found that certain concentrations caused precipitates to incline towards the crystalline state, while with greater or less concentrations the reacting liquids formed crystals always less distinctly, until finally these could not be identified even under the microscope. With certain solution concentrations, then, crystal formation may be observed; at lower concentrations than those tending to crystal formation, the magnitude of the crystals continuously decreases with in-



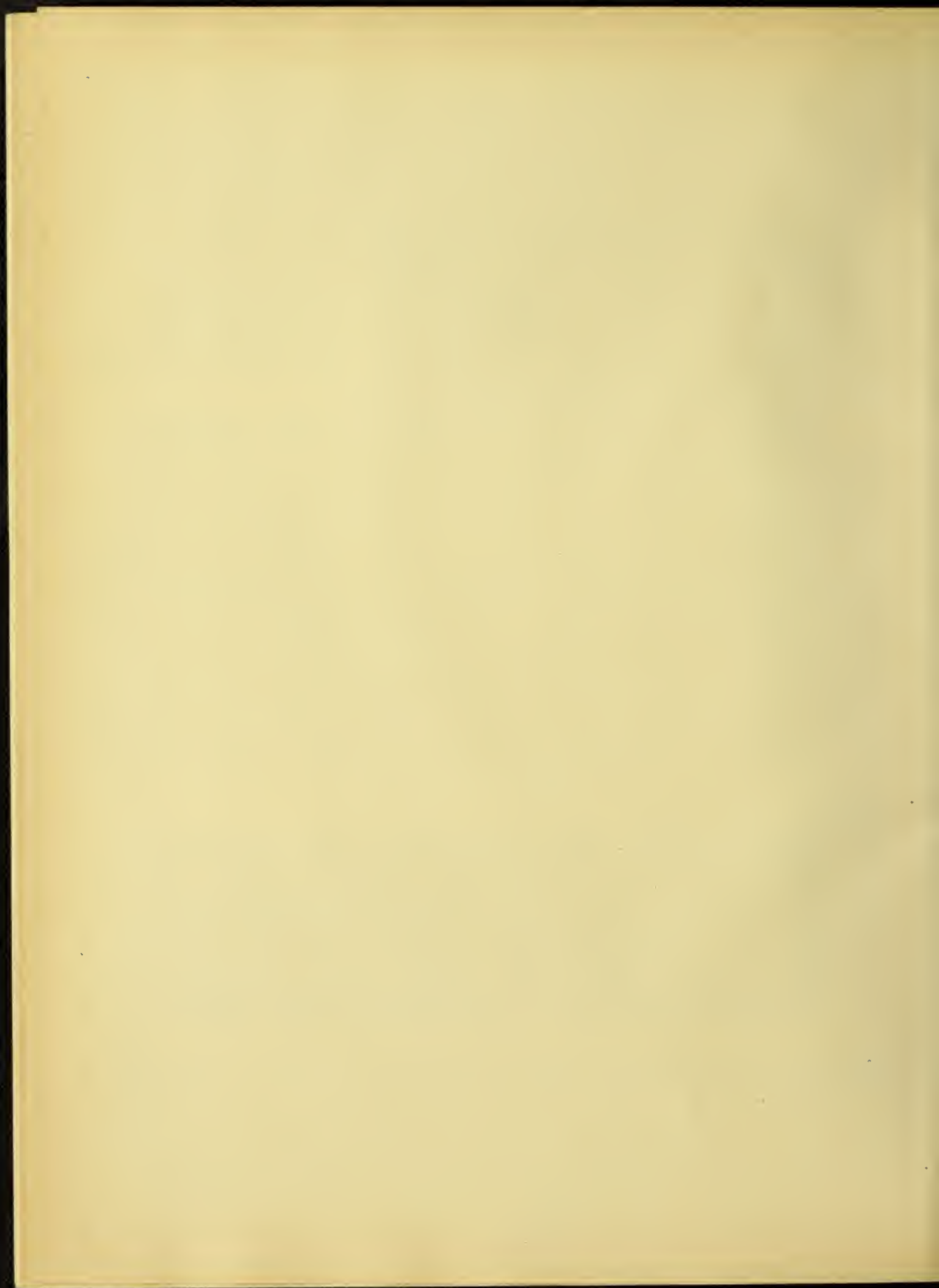


The colloidal portion of clay may consist of organic residue and finely divided or colloidal carbon in varying proportions in addition to inorganic colloid minerals of clay and these exert a marked influence on the adsorption and absorption of soluble and insoluble salts as well as on the absorption of other colloidal substances. The removal of voluminous and gelatinous substance from clays by Th. Schloesing<sup>1</sup> and others has led to quite conclusive proof that colloidal substances exist in clays.

Although the substances in the colloidal state contained by clay are only small in quantity, such properties of clay as plasticity, absorption etc., may still be attributed to the influence of such colloidal substance, and this is the greater the more homogeneously it is disseminated throughout the mass of clay grains as is the case with clays having a large surface factor. As the mineral particles of clay approach the size of molecules, the mass becomes more continuous and the colloid content becomes more effective as a lubricant in developing plasticity. The mass is more flexible  
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continued from page 3.  
creasing dilution, until finally what we term colloidal solutions arise; it is, therefore, probable that the smallest particles - viz., the ultra- and a -microns possess a crystalline character. The disperse phase of suspensoids has, in addition, the ability to bring about the supersaturation of molecular disperse solutions; a- and sub- microns in contact with their dispersion medium have the ability to stiffen into microcrystalline structures. Finally, many optical properties support the assumption of a crystalline disperse phase (e.g., the scattering of colour in the ultramicroscopic image).

1.  
"The Const. of the Clays." Compt. Rend. Vol. 79, 1874, p. 376-80, 473-77.

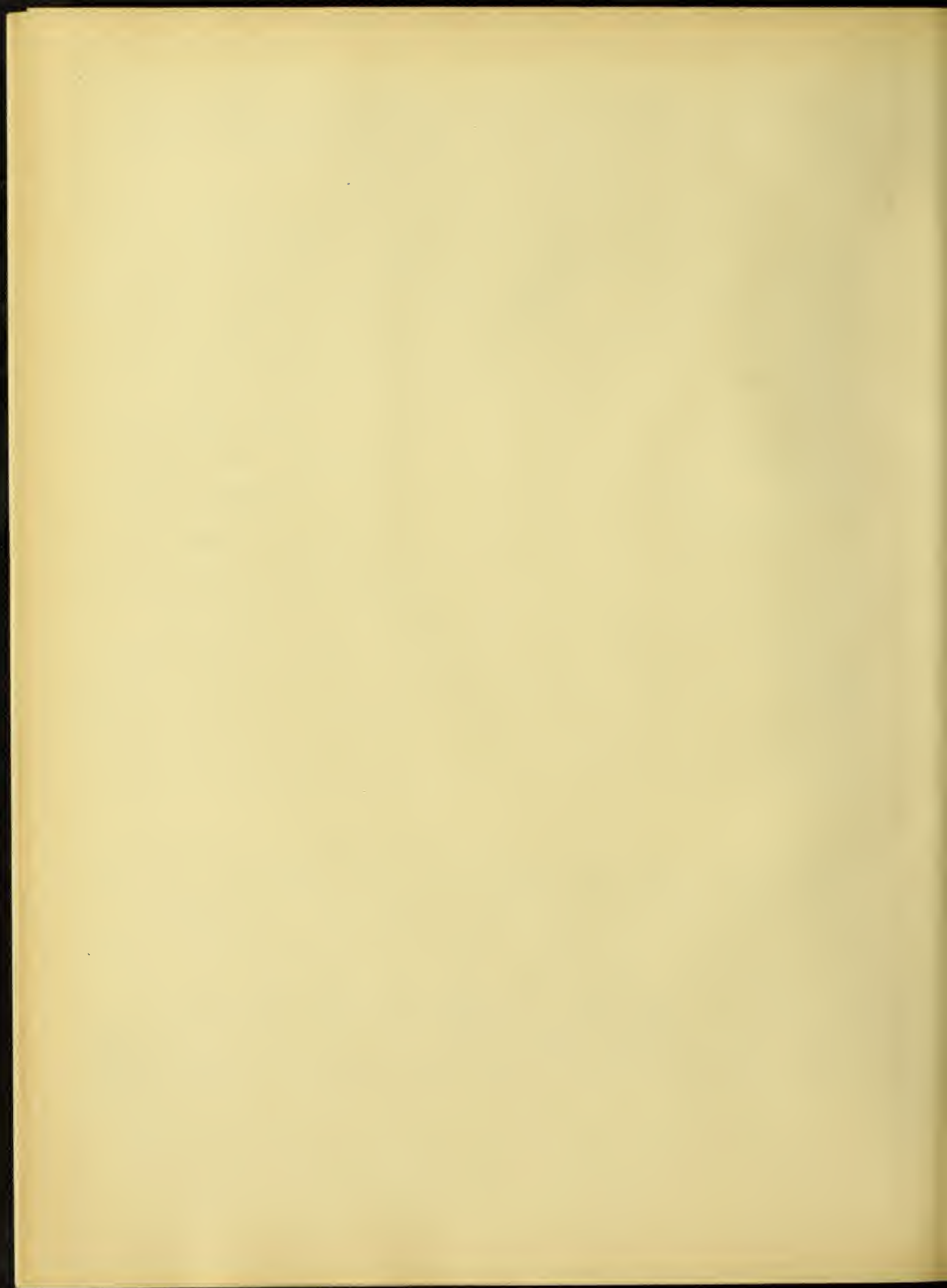




and subject to deformation without destroying the cohesive and adhesive forces of the molecules. The more coloring dye is adsorbed due to the increased area of surface.

Purdy and Moore<sup>1</sup> consider it "an exceedingly probable assumption that it is the influence of the adsorbed salts that gives to clay its plasticity." Adsorbed salts certainly help the plasticity because they gelatinize the colloid content of the clay and thus make it more mucilagenous by increasing its adhesive power. The salts may also put the dispersion medium in a better condition for colloidization of the clay minerals. Schloesing,<sup>2</sup> Van Vermelen,<sup>3</sup> Rohland,<sup>4</sup> Cushman,<sup>5</sup> Purdy,<sup>6</sup> Ashley<sup>7</sup> etc. give interesting papers with reference to colloidal substances in clays as a cause for their plasticity. F. F. Grout<sup>8</sup> and F. Poppe define plasticity as a double property, involving both capability of flowage and strength and conclude that it must have a cause to explain both factors. Then after reviewing and explaining the molecular Attraction Theory and the Colloid Theory of Plasticity and stating that molecular attraction will vary, both with the nature of the solid

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1. "Pyrophysical & Chemical Behavior of Clay. Trans. Am. Cer. Soc. vol. 9, 1907, page 222.
  2. The Constitution of Clays: Compt. Rend., Vol. 79, 1874 pp. 376-380, 473-477.
  3. Chem. Zentralblatt (1882) n. 1255; z.f. anorg. chem. 18, p. 14 (1898); 23, p. 321 (1900)
  4. Zeitschrift f. anorg. chem., 1902, 158; 1904, 325.
  5. J. Am. Chem. Soc. 1903, 451; Trans. Am. Cer. Soc. 6, 65.
  6. Bull. #9 Ill. State Geol. Survey
  7. Bull. 388, U.S. Geol. Survey; Trans. Am. Cer. Soc. Vol. 12, p768
  8. "The Plasticity of Clay," Trans. Am. Cer. Soc. Vol. XIV, 71-81.



and with the nature of the solution, and also admitting that colloids are certainly present and necessarily active, they wish to belittle the importance of the colloid theory by considering the colloids a minor factor in the production of plasticity in clays because they consider colloids quantitatively insufficient and also because they have not succeeded in making a non plastic powder as plastic as clay by the use of colloids. It occurs to me that the molecular attraction exists with increased strength enough to exhibit plasticity because of the presence of clay minerals in the colloid state, those attractive and binding forces taking effect between the colloidal particles and aggregates as well as between the clay grains without any regard for the colloid state of the latter. Therein would lie a cause for Grout's double property in plasticity - the colloid clay minerals as a lubricant making the flowage of the clay possible and as an adhesive gelatinous substance making the property of strength possible. Also, some of the colloids are in the soluble state as "Sols", and may add to the binding forces giving the mass strength.

In discussing Size of Grain Theory of Plasticity, R. C. Purdy<sup>1</sup> quotes H. B. Fox where the latter says that, "Plasticity varies directly with the fineness of grain of a shale." And he also states that, "it is not mere assumption that the finest particles in clay are the purest kaolin grains." These citations seem to present the existence of conditions which are highly conducive to the formation of dissociable, electrically charged, colloid molecules to which we

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1. Ill. State Geol. Survey, Bull #9, page 182.





can attribute the cause for plasticity on account of molecular attraction forces. With substances other than clay minerals the mere presence of fine particles is not sufficient to cause plasticity unless colloid molecules are developed. Potters flint (dry ground) is finer grained than most clays, yet it does not exhibit the faintest sign of plasticity. Professor Orton<sup>1</sup> found that, "glass particles which were so fine that they remained in suspension for hours without settling, when collected exhibited no plasticity." Fineness of grain then seems only to be a required condition in the operation of the real cause of plasticity. To quote Wheeler,<sup>2</sup> "while it is true that fine clays are usually very plastic and coarse clays much less so, there are very many exceptions." Mr. Gault<sup>3</sup> says, "That while the majority of clays improve on fine grinding, some are unchanged." The lack of the colloidal form of clay minerals could explain these two cases. The questions of fineness of grain and the shape of the particle become largely but modifying factors rather than determinants of plasticity.

Adsorption and absorption phenomena are not causes of plasticity but rather a resultant property due to colloidal mass structure and molecular attraction forces just as plasticity is also a resultant property of these. These molecular attraction forces are associated with molecules of liquid, hydrated solid molecules or particles and solid particles alone. The hydrostatic forces apply to the colloid-sol system and the molecules of the dispersion medium in the form of surface tension, which is the cohesive force

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1. Brick, Vol. XIV, No. 4, page 216.

2. Loc. cit. page 109. (Ill. State Geol. Survey Bull. #9 p. 186.

3. W. Va. Geol. Survey, Vol. 3. page 46.

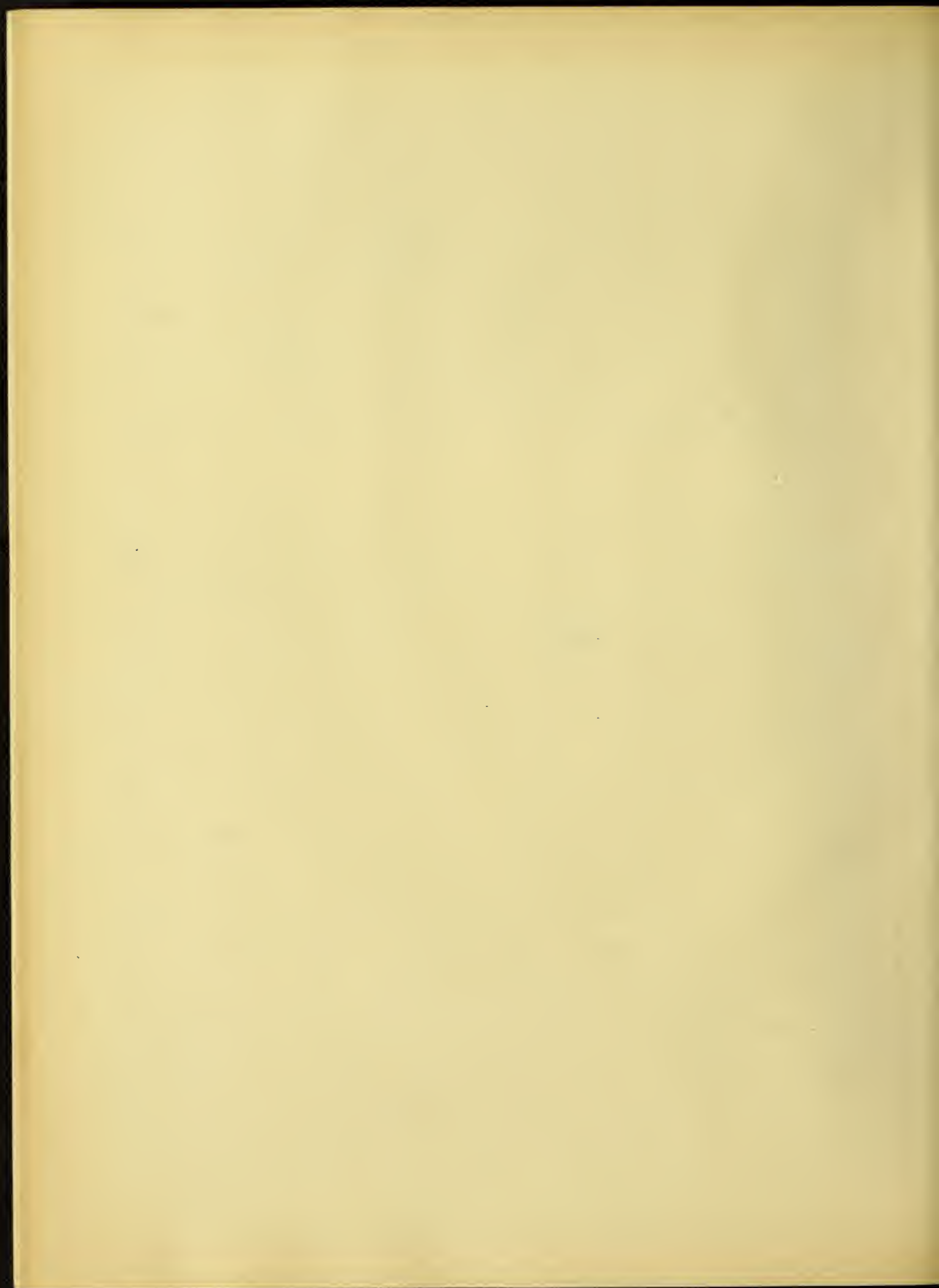




which one particle has for another of its kind; and in the form of adhesive forces between the molecules of different composition as those of crystalline solution, colloidal solution, and the more solid particles as colloid gels and crystalline mineral grains; and in the form of surface pressure of the particles making up the solution or dispersion medium. Again, forces which are probably included in the foregoing, exist between the molecules, both solid and liquid, due to the electrostatic charge of their ions, and the water films combined with these ions most probably have opposite charges.

"The<sup>1</sup> practical conclusion from the discussion of molecular attraction forces of interest in connection with plasticity, is that when the surrounding fluid has the greater potentiality (molecular attraction), flocculation or drawing together of the solid particles will result. When the solid particles have the greatest potentiality, deflocculation or separation of the solid particles will result." "The surface tension of solutions which cause deflocculation of grains of pure clay substance is without exception lower than the surface tension of water." Physical conditions, such as concentration of the solution, temperature, etc., which tend to decrease surface tension in the solution, increase the deflocculating power of the solution. "Solutions which have surface tensions higher than that of water tend to cause flocculation. But depending on the solid substance, solutions of lower surface tension may cause flocculation." In the same bulletin, Purdy says, "On putting together the known facts concerning clay and water, it is evident that the film of water surrounding the

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1. R. C. Purdy, Bull #9. Ill. Geol. Survey, page 191.



grains of clay (when the mass is in a plastic condition) has a very high potential, owing to the high degree of concentration of the salts that are held to the kaolin grains by adsorption." But what is the cause of this strong adsorption? Colloid gels by virtue of their micellian structure!

Present methods of experimentation are hardly sufficiently perfected to be able to demonstrate the cause of plasticity in clay. However, if we consider the laws and theories of certain branches of physical chemistry, they, in cooperation with the known facts which support them, should help make clear for us the cause or causes of plasticity. It appears that both remote and immediate causes can be discerned, the immediate causes having arisen as results of the remote causes. The intrinsic properties of the clay minerals and the colloidization of these mineral grains or crystals by weathering processes constitute the remote causes. The molecular attraction forces between molecules of a kind and those different, which are considered because of our accepted theories of "Molecular Structure" of matter, ("matter" - discontinuous, micellian, or mesh-like in structure) and "Electrolytic Dissociation," which manifest themselves in the clay as absorptive, adsorptive, shrinkage, and crystallization forces and tensions may be considered as the immediate causes. Thus the molecular attraction theory by virtue of the existence of the colloid form of matter, manifests its truths in clay by exhibiting the properties we call Plasticity, Adsorption, Absorption, and Shrinkage.

Some essential criteria<sup>1</sup> of a "Suspension colloid" are:

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1. We. Ostwald, Grundriss der Kolloid Chemie, Dresden, 1909.





- I. The viscosity varies very little from that of the pure dispersion medium.
- II. The existence of a distinct electric charge capable of detection. On the addition of electrolytes, coagulations take place which are irreversible.

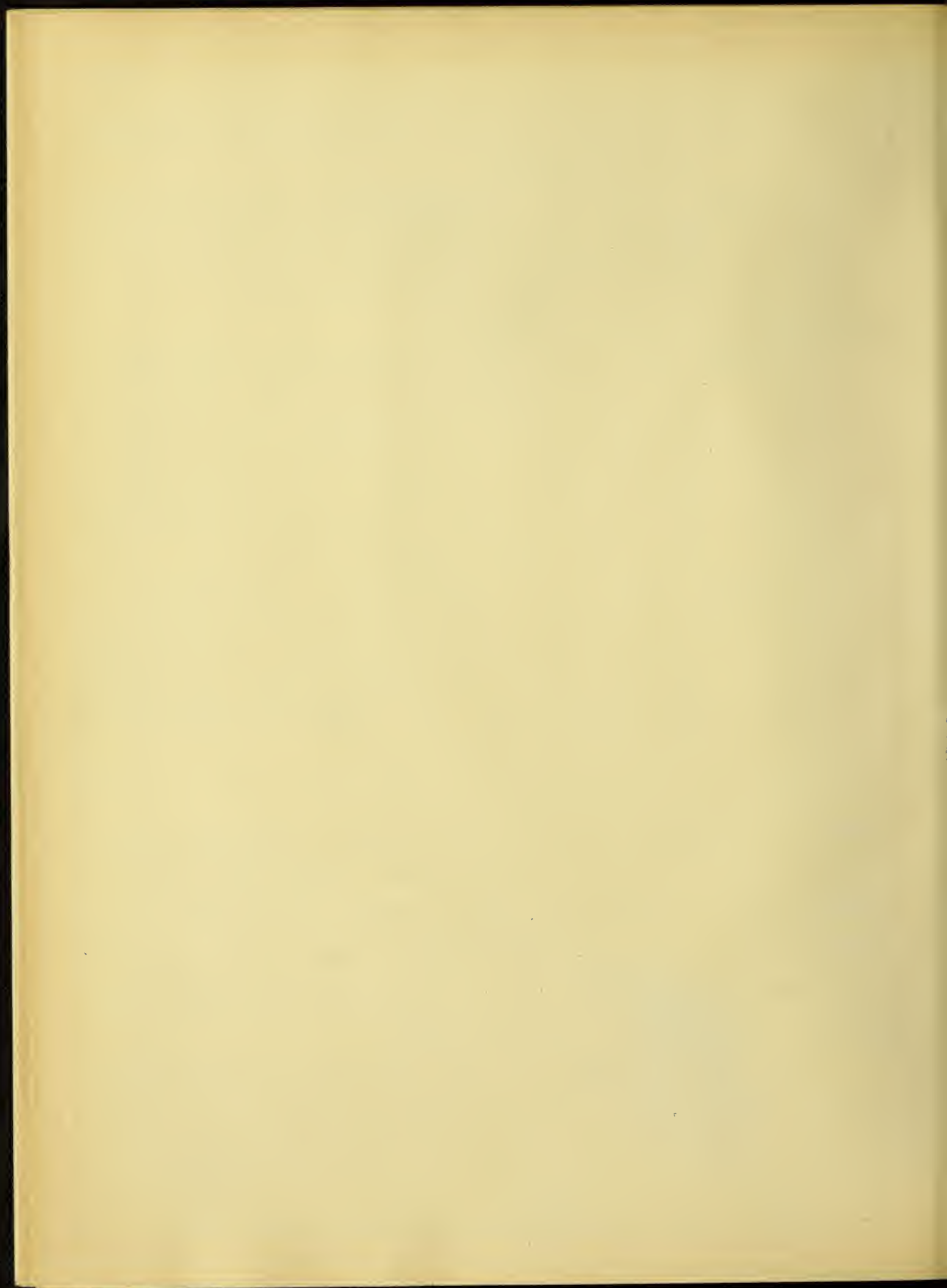
The same of an "Emulsion Colloid" are:

- I. The large internal friction (viscosity); even a small concentration essentially increases the viscosity of the dispersion medium. The rise in viscosity takes place with enormous rapidity as the concentrations become greater. With rise of temperature the value of the internal friction sinks appreciably.
- II. The absence of electrical phenomena. Cataphoresis is at the most only feebly observed, and the coagulation only takes place by the addition of salt solutions of great concentrations. The products of coagulation are very similar to liquids.
- III. Ability to gelatinise and swell.

From the above criteria it would seem feasible to consider a clay mineral colloid as a sort of medium between a suspension colloid having a solid disperse phase, and an emulsion colloid having a liquid disperse phase. V. Pöschl<sup>1</sup> seems to think that the best explanation of the colloidal state is obtained by a union of the adsorption theory with the suspension theory.

If it can be concluded that the first cause of plasticity is colloid formation, may we not find a means of measuring the viscosity of this colloid form of minerals in a clay and then incorporate

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 1. V. Pöschl- "The Chemistry of Colloids," page 88 and 94-95.





this factor in Mr. H. E. Ashley's<sup>1</sup> plasticity formula to obtain a better series of numerical plasticity values for different clays? The viscosity of the clay sample, washed free from salts as far as possible, as determined by an efflux method would probably suffice to obtain such a factor, "V". The formula would then become, 1

$$P = \frac{B \times C \times V}{A}, \text{ where}$$

P = the numerical value of plasticity, to be calculated

B = The cast air shrinkage

C = The relative colloids, determined by dye adsorption.

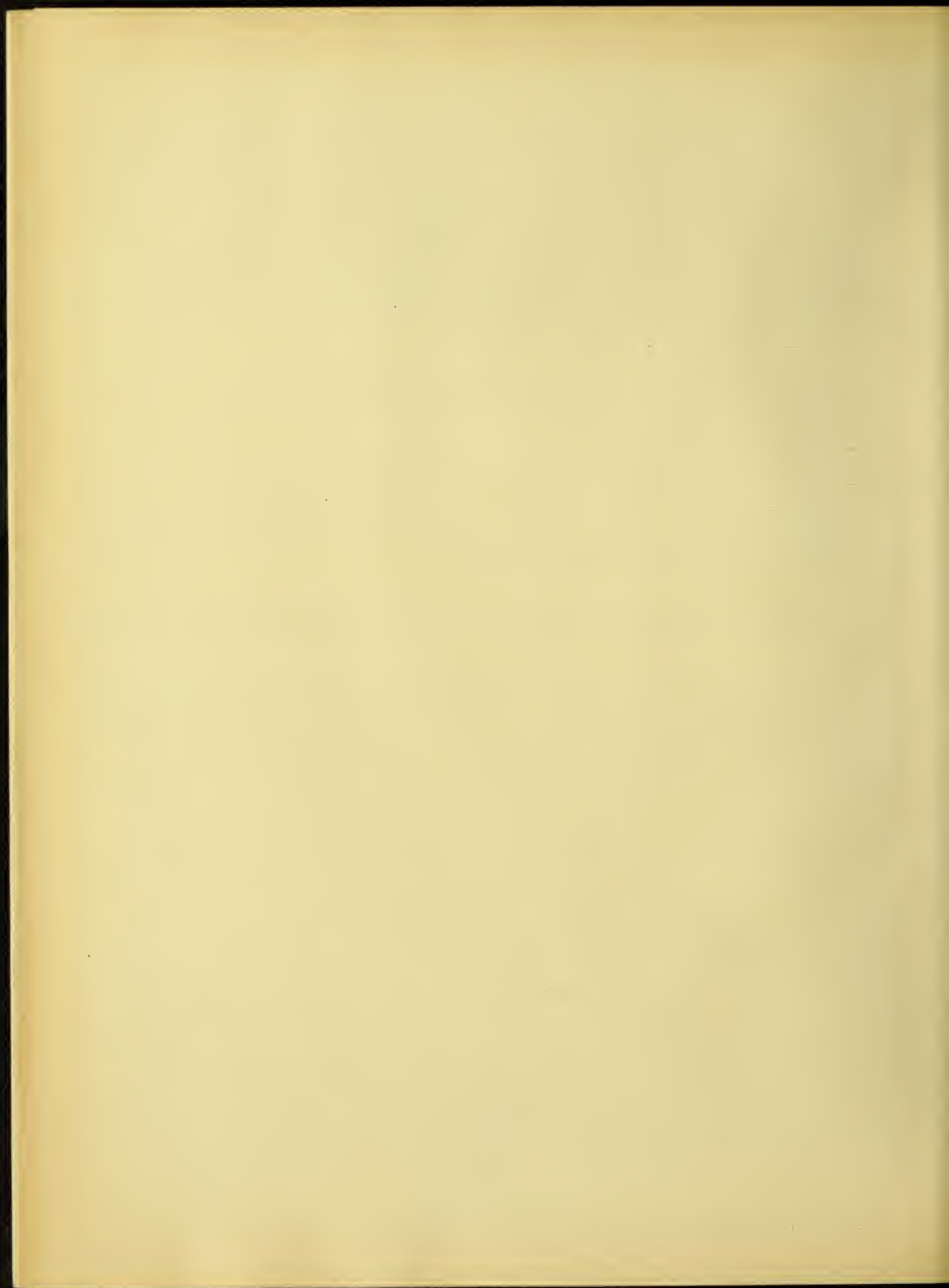
V = Viscosity value of a selected weight of water and dried clay

A = The Jackson-Purdy surface factor.

## II. The Effect of Electrolytes Upon Clay In the Plastic State.

In view of the fact that practically no results are available in the literature concerning the effect of electrolytes upon clays in the plastic state, it was decided to make a careful attempt at obtaining some numerical values of this kind. The volume shrinkage of bricks resulting from drying under constant conditions was used as the criterion for measuring the effect of electrolytes upon clay in the plastic state. This was done because it is widely believed that any salt which will either change the surface tension of the liquid medium and consequently its viscosity or would affect a change in the state of the colloid content of the clay, will manifest such effects best in the variation of volume shrinkage. It is known that shrinkage is a function of plasticity and the latter is intricately associated with the amount and kind of liquifying

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1. Bull. #388. U. S. Geol. Survey. 1908.

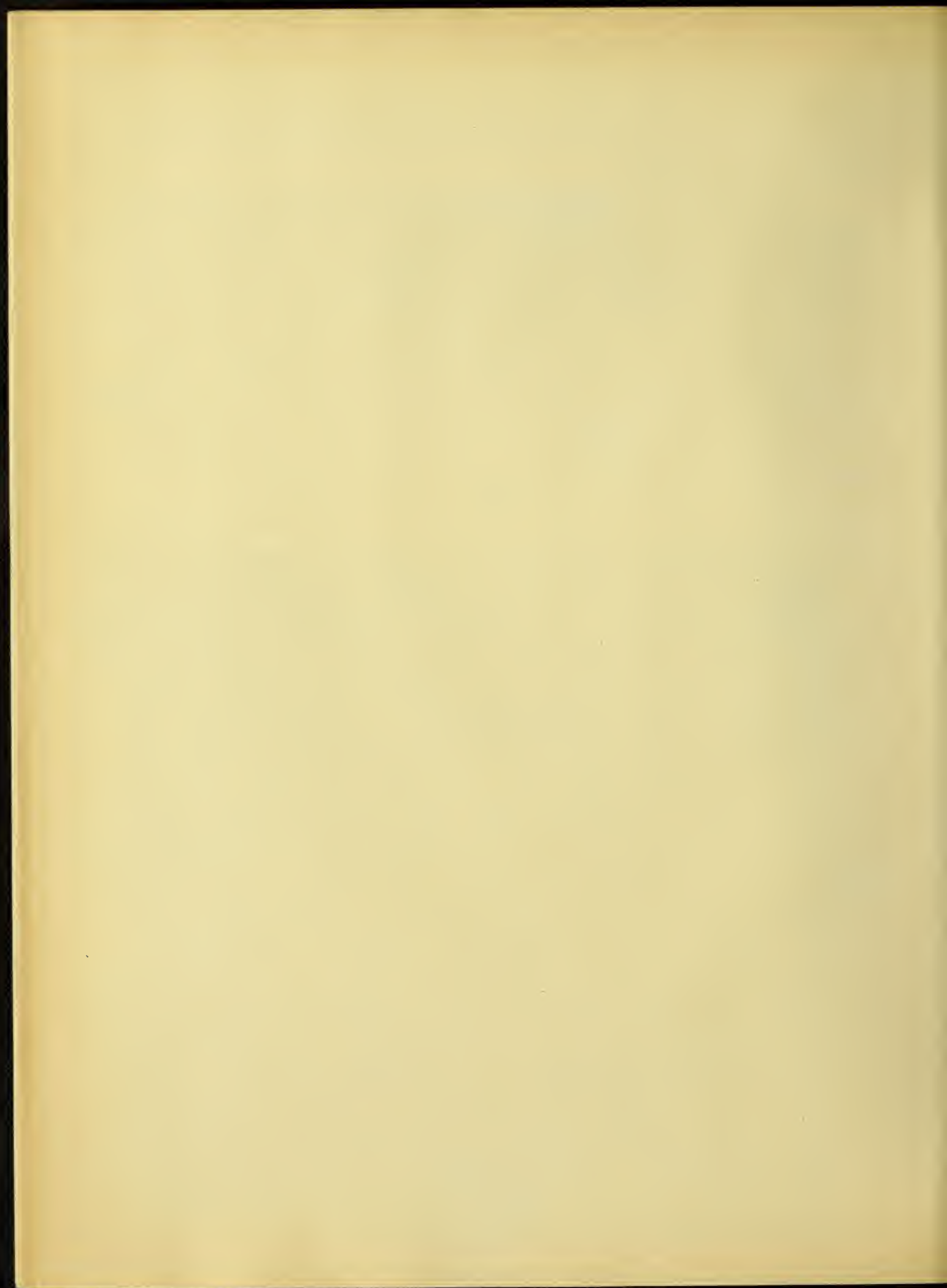


medium as well as the physical and physico-chemical condition of the clay constituents.

The method of procedure consisted in preparing a thoroughly mixed sample of the clay, drying portions of this quantity at  $110^{\circ}\text{C}$ , allowing the dried clay to cool in a desiccator, and then weighing out sufficiently large portions to make up with given weights of salts and water into plastic masses for molding brickets. After preparing a thoroughly<sup>1</sup> worked mass of the desired plastic consistency, it was stored in a moist chamber for twenty four hours in order to make reasonable allowance for any time effect.

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- 1."The following will help explain the extreme irregularity in the curves of plates #6 and #7, for Tennessee Ball Clays #1 and #7. The ball clays were not always dried in constant quantities nor for equal lengths of time although the temperature was maintained between  $105$  to  $112^{\circ}\text{C}$ . The water plus salt solution used in making a plastic batch was always kept at constant volume and used with a constant weight of dried clay, but the mixing of water and clay, although the best that could be decided upon at the time, was not the most satisfactory. It is probable that the method of procedure adopted is mostly responsible for the irregularities in the measured shrinkages of brickets with varying salt concentrations used. The mixing was done by hand with the aid of a steel spatula on a piece of sheet zinc. It is evident that in mixing the clay, ample opportunity was afforded for water evaporation from the mixture and salt absorption by the clay from the moist skin of the hand which would certainly introduce irregularity in results. The effect of time for mixing and kneading the plastic mass was not taken seriously into account for the two ball clays, which is another cause for irregularity in the results obtained. This work was carried on for a period of about 3 months which allowed a considerable temperature variation in the spring of the year to exert its influence thus introducing error in the mixing process. Each plastic batch made contained sufficient material for two brickets and from the fact that the brickets for the individual batches check reasonably close in volume shrinkage, we know that but a slight error was introduced in the volume measurement. When the work with Georgia Kaolin and  $\text{NaCl}$ ,  $\text{CaCl}_2$ , and  $\text{AlCl}_3$  was begun, all the processes were carried out with great care in regard to the foregoing errors and the possibility for introducing irregularities was guarded against as far as practicable for the methods used. This was gratifying as shown by the results given on plate #2. The value of these results are greatly enhanced because of their consistency with such crude methods as had to be adopted for mixing and kneading."





The clay in the plastic condition was molded in a brass form into bars 10 x 2.5 x 1.56 cm. which were at once weighed and then immersed in petroleum until its volume was measured in a voluminometer a few hours later. For each concentration of salt, three bars were made and measured. The specimens were then allowed to dry at the laboratory temperature for three days after which time they were heated in an oven regulated by a thermostat to  $110^{\circ}$ , to constant weight. The dry bars were at once weighed and immersed in petroleum until completely saturated when they were placed in the voluminometer for the determination of the dry volumes.

In order to establish the limits of the working consistencies of the clays used, samples of the clays were made up into bars representing the extremes of the plastic state, i.e., so dry at one end of the series that the mass could barely be worked and as wet at the other end as the clay would permit. The drying shrinkages were then determined as usual. The results of this work are given on plate #1. These curves illustrate the short range of working consistency of the two kaolins as compared to the much longer range for the ball clay. For the full line curves the per cents of water are calculated from the wet and dry weights of the bricks while for the broken line curves the per cents of water as actually added to the clay in mixing, was used. It is evident that the plotted points which show crosses are more or less in error. It is interesting to note that the curvature of the N. Carolina kaolin curve differs from that for the Georgia kaolin and the ball clay, showing that for a given increase in per cent of water, the latter two clays show a greater increase in volume shrinkage over the N. Carolina kaolin, especially for the higher per cents of water used

1890  
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1892  
1893  
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1900



Curves For Three Clays  
 Showing Relation Between Volume Shrinkage  
 And Water Content When Water Is Varied  
 From Minimum To Maximum Per Cents  
 For Working Clay In The Plastic State.  
 Full-line curves -  $H_2O$  calculated from Wet & Dry Weights.  
 Dash-line curves -  $H_2O$  accurately added to make plastic.

Per Cent Volume Shrinkage on Dry Volume

44  
42  
40  
38  
36  
34  
32  
30  
28  
26  
24  
22  
20  
18  
16  
14  
12  
10

Tennessee Ball Clay #1.

Tennessee Ball clay #1

Georgia Kaolin.

Georgia Kaolin

N. Carolina Kaolin.

N. Carolina Kaolin

PLATE I

Per Cent Water By Weight on Dry Weight.

30 32 34 36 38 40 42 44 46 48 50 52 54 56 58

Robert Back - 4/6/18.



for each clay. It is also noted that for any given volume shrinkage there is a much greater difference between the per cent water on the full line and broken line curves for N. Carolina kaolin than there is for the Georgia Kaolin curves. It is a difference of about 4% for N. Carolina Kaolin which is nearly as much as the greatest difference for the ball clay curves, thus showing that for the highest percentages of water used for each clay, about 9.45% of the total percent water of the N. Car. kaolin is retained as hygroscopic and pore water, while for the lowest percent water, the amount is 9.75%. The respective figures for Georgia Kaolin are 4.5% for the highest and 4.7% for the lowest while for Tenn. Ball clay, they are 10.85% for the highest and 5.00% for the lowest.

That there should be little or no variation in the two figures for both of the kaolins and such a marked difference for the ball clay, indicates a radical difference in structure. It is also noted that the per cent hygroscopic and pore water for the N. Car. Kaolin is more than twice that for the Georgia Kaolin, a fact which is most probably the cause for the difficulty in fitting a "clay slip" containing N. Car. Kaolin to a clay body. The middle point of each curve stands for the most satisfactory molding condition in each case. Taking this point in the ball clay curve and the Georgia Kaolin curve, it is observed that the ratio of per cents water is  $48 \div 36.4 = 1.32$  while the ratio of volume shrinkages is  $31.6 \div 15.2 = 2.08$ .

On plate #2, the curves show the effect of  $\text{NaCl}$ ,  $\text{CaCl}_2$  and  $\text{AlCl}_3$  upon the volume shrinkage of Georgia Kaolin. It is noted that both the  $\text{CaCl}_2$  and  $\text{AlCl}_3$  are more effective than  $\text{NaCl}$  in amounts less than 0.04 percent. With a content of 0.05 per cent, the

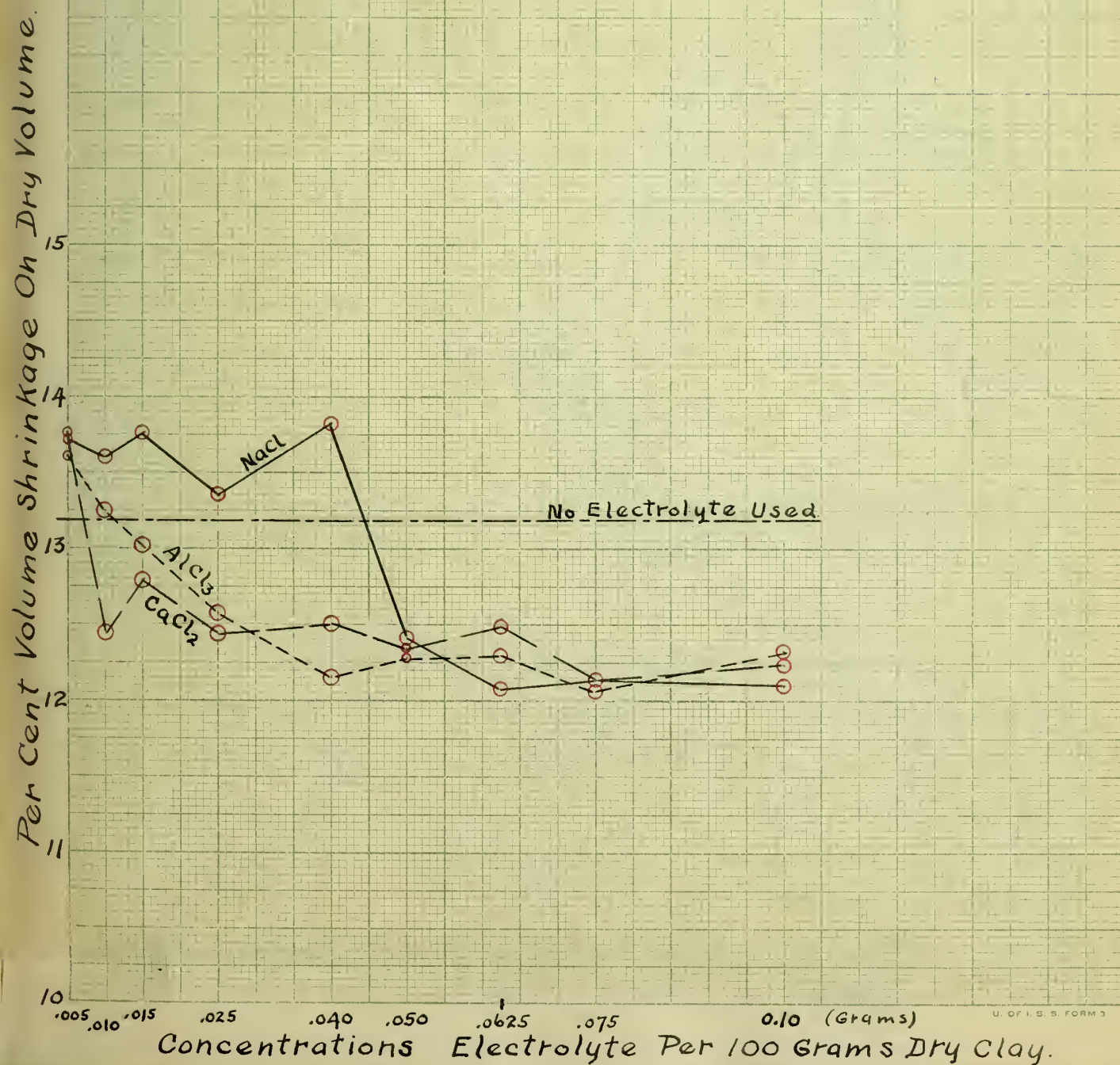


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CITY OF LONDON

## PLATE 2.

## Curves

Showing Influence OF Electrolytes  
Upon Volume Shrinkage For Georgia  
Kaolin In The Plastic Condition.



Robert Back 4/6/13.



sodium salt brings about the same decrease in shrinkage as smaller amounts of the other chlorides. The interesting fact is that 0.005 per cent of any of these reagents, maintaining the same amount of liquid, cause approximately a half per cent increase in shrinkage above that for the same volume of water. Kleininger<sup>1</sup> says "that the cause of the dual behavior of the electrolytes is to be sought in dissociation phenomena." The following explanation is offered by the writer: The slight increase in shrinkage for the smallest per cents of electrolytes used can be attributed to the fact that, these smallest additions of electrolytes lower the surface tension of the liquid medium used sufficiently to make the volume of the same more than enough to obtain the same degree of plasticity as with distilled water alone for the liquid medium. Deflocculation of purest clay grains takes place when the surface tension of the liquid medium is less than that of pure water. Consequently, the shrinkage must be raised over that represented by the dash and dot line until the concentration of electrolytes reaches a point where the surface tension of the liquid medium is higher than that of pure water and the first effect becomes over-balanced. The liquid of higher surface tension exerts its influence by coagulating or flocculating the colloid content of the clay with consequent decrease in shrinkage for the same volume of liquid medium used.

The dissociation of the salts and the results of their electrolytic phenomena do not begin to show appreciable effects until we deal with clay in more dilute solutions as shown in another part of this work. According to Rohland, such chlorides as  $\text{NaCl}$  and  $\text{CaCl}_2$  should be entirely neutral, but the work here seems to

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 1. Original Communications, 8th Internat. Congress of A.C. vol. V. 24



indicate that they are quite active in affecting the efficiency of the liquid medium to exert its influence and, with clay in the suspended slip state, they display decided activity.

"The use of NaCl is of special interest in this work on plastic clay", Prof. Bleininger<sup>1</sup> states, "since experiments carried on in this laboratory showed that in the case of exceedingly plastic clays of tertiary origin the plasticity was greatly decreased by the use of salt solution which was strikingly demonstrated by their drying behavior. Brickets made from the untreated clay cracked and checked very badly while specimens made up with a NaCl solution dried normally without the slightest evidence of cracking and at the same time possessed a greatly reduced drying shrinkage."

In order to show to what extent the relation between shrinkage and pore water is affected by the use of these reagents the total and shrinkage water were calculated in terms of the true clay volume. For this purpose the density of the powdered clay was determined by means of the pycnometer under the usual precautions. The volume of the shrinkage water was then calculated from the evident relation:

$$\frac{100 (V_1 - V_2)}{w/d} = \text{per cent shrinkage water (by volume)}$$

where  $V_1$  = volume of wet bricket.

$V_2$  = " " dried "

w = weight of bricket dried at 110°C.

d = density of clay.

Similarly,  $\frac{\text{Total water (c.c.)} \times 100}{w/d} = \text{per cent total water (by vol)}$

.....

1. Original communications-8th Internat. Congress of A. C., Vol.V.p 24





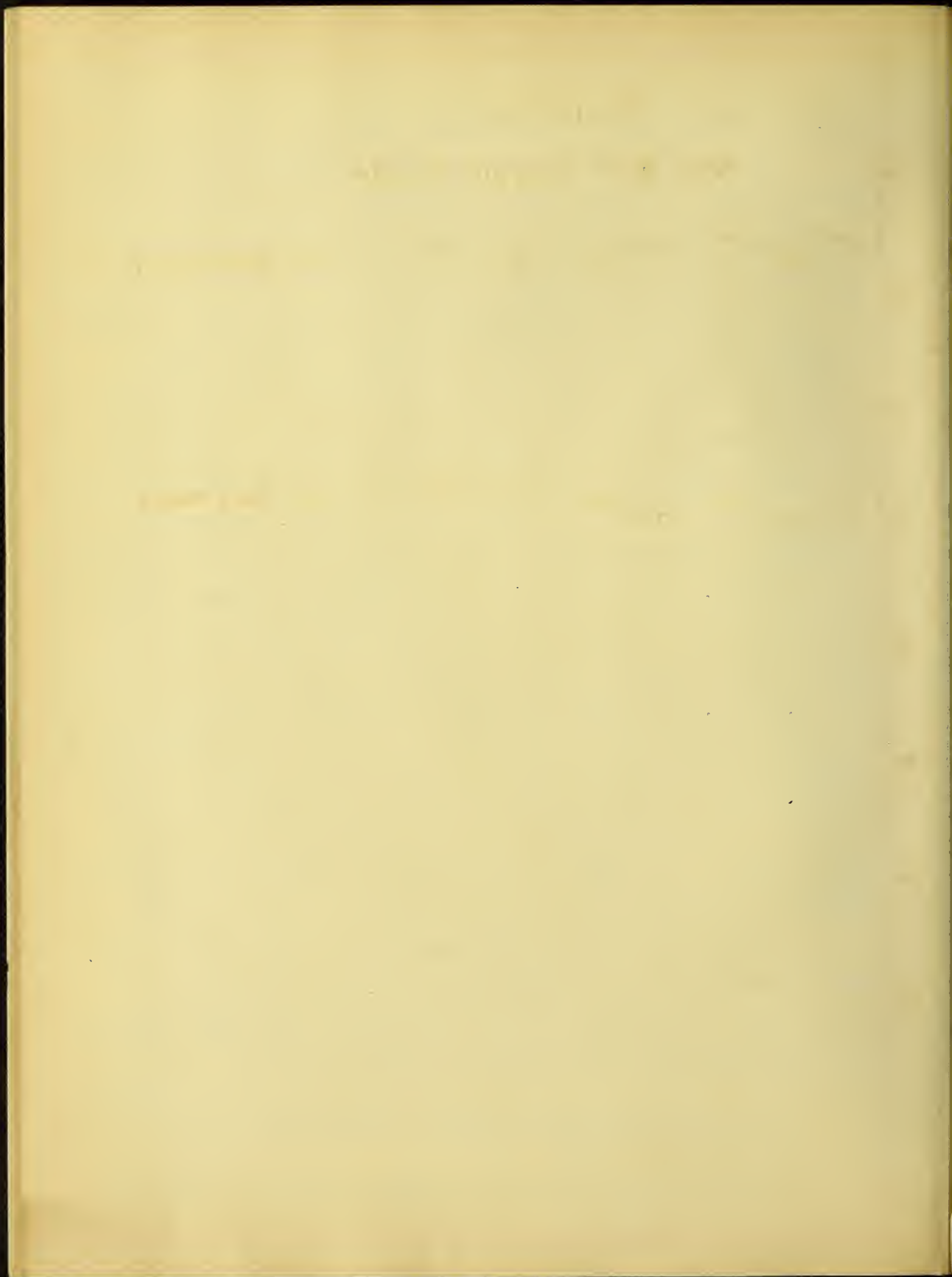
and, total water minus shrinkage water equals the pore water.

In plate #3, this relation is shown graphically for the addition of NaCl. It is seen that the shrinkage water volume was first increased and then slightly decreased. The decrease is due to a drop in the total water content and a rise in the pore water curves. This same relation for  $\text{CaCl}_2$  and  $\text{AlCl}_3$  upon Georgia Kaolin is shown graphically by plates #4 and #5 respectively. In these three plates the addition of salts affects the shrinkage water volumes by decreasing them from 10 to 11% of the average for no salt used and the same affects the pore water volumes by increasing them from 3 to 4% of the average for no salt used. However, the per cent pore water volume for  $\text{AlCl}_3$  on plate #6 does not show this increase very markedly. Since the wet and dry weight of bricks do not vary by more than one per cent among themselves respectively, and since volume measurements for duplicate pieces did not vary by more than 0.2 to 0.6% it seems justifiable to attribute these varying shrinkage and pore water volume relations to an arrangement of the clay particles affected by these reagents or to a change in their power for holding water which will not evaporate at  $110^\circ \text{C}$ . The latter change is affected by the reagents in changing clay Sols to Gels which increases the absorptive power of the clay for water.

On plates #6 and #7, results are shown graphically for the effects of NaCl,  $\text{CaCl}_2$  and  $\text{AlCl}_3$  upon Tenn. Ball Clays #1 and #7 respectively in the plastic state. The note of page #12 explains the irregularities in the curves for plates, #6 and #7.

### III. Electrolytes with clay as a Thick Paste.

On plates #8 and #9 are given graphic results illustrating

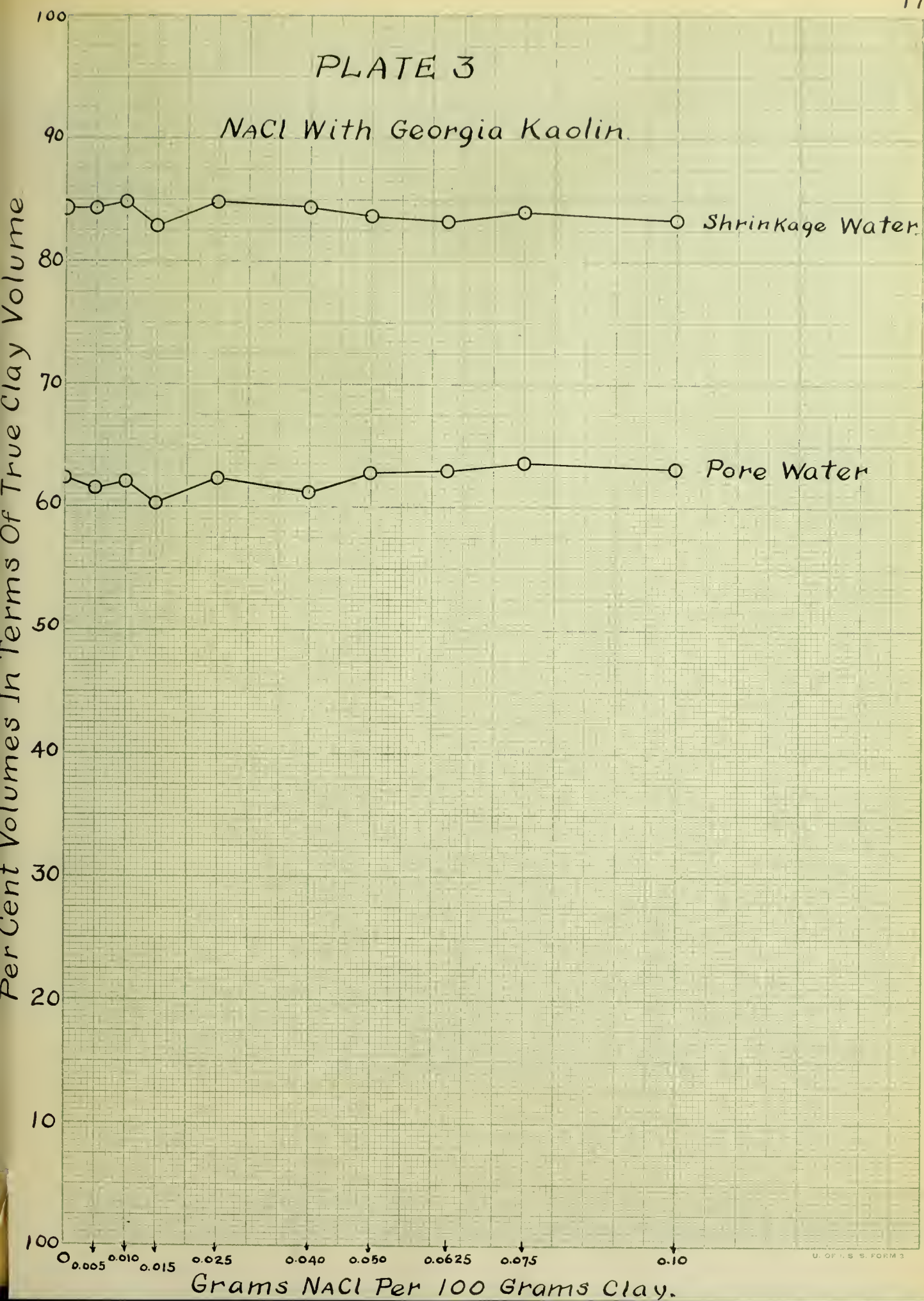


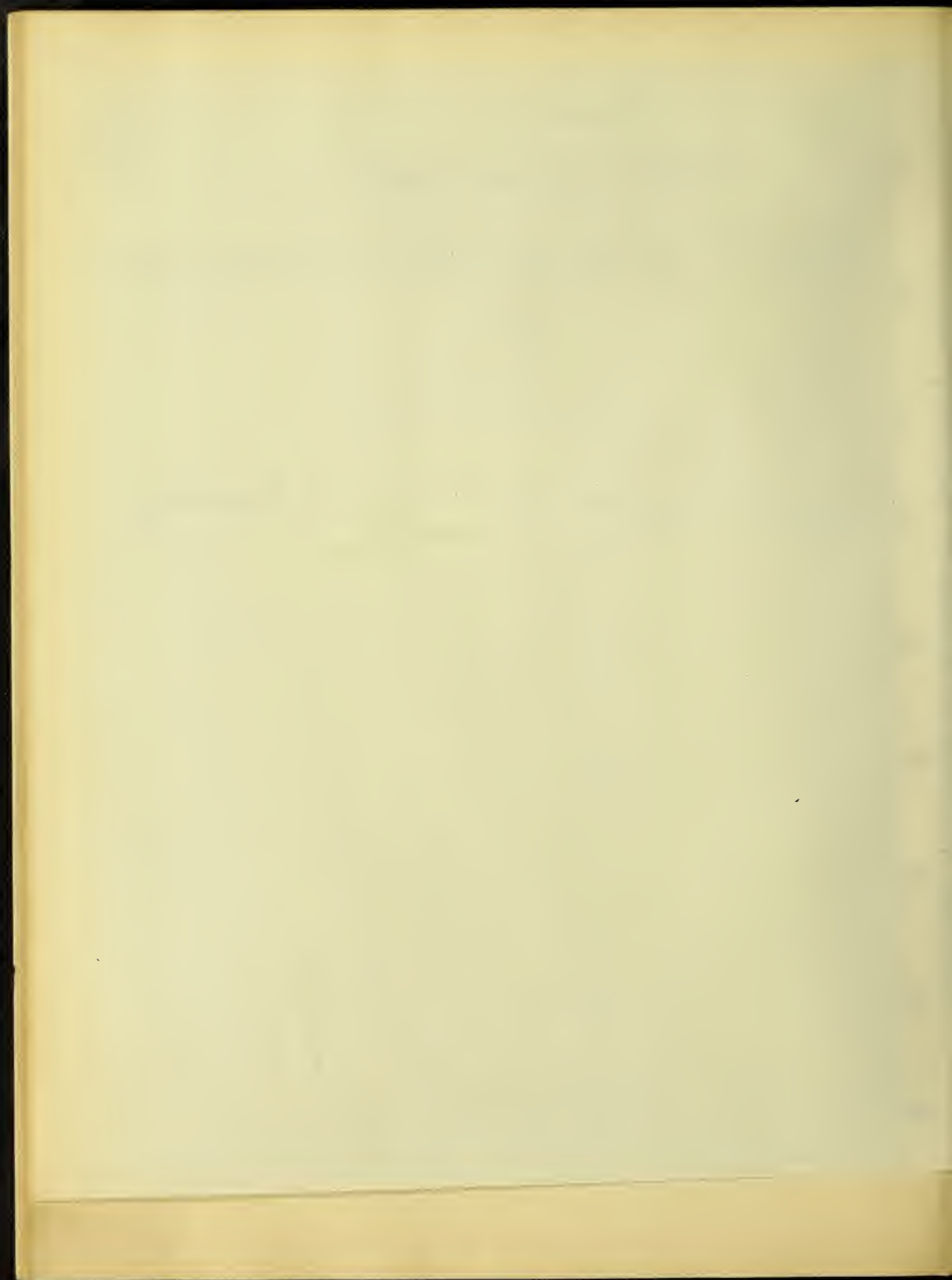


## PLATE 3

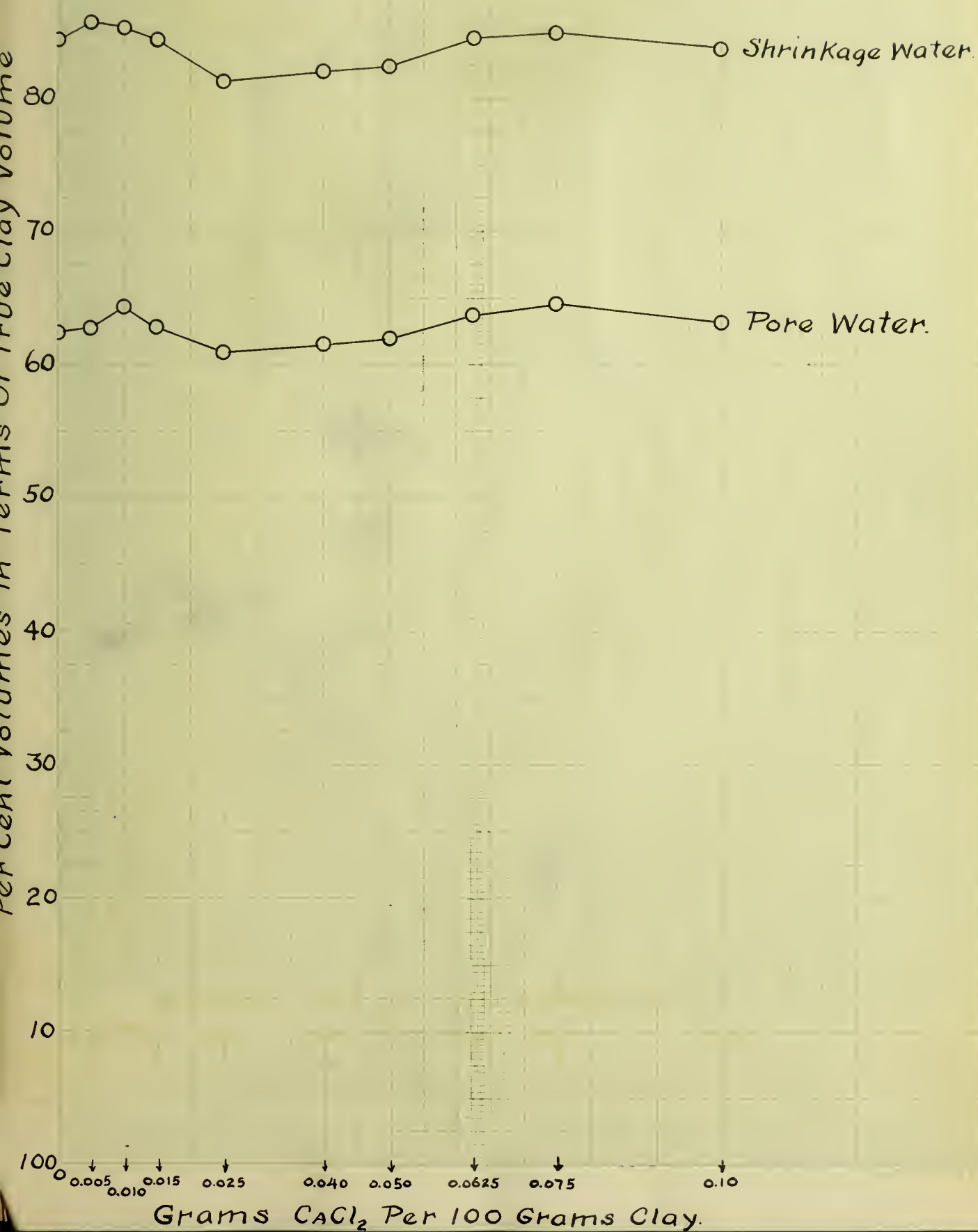
NaCl With Georgia Kaolin.

Per Cent Volumes In Terms Of True Clay Volume

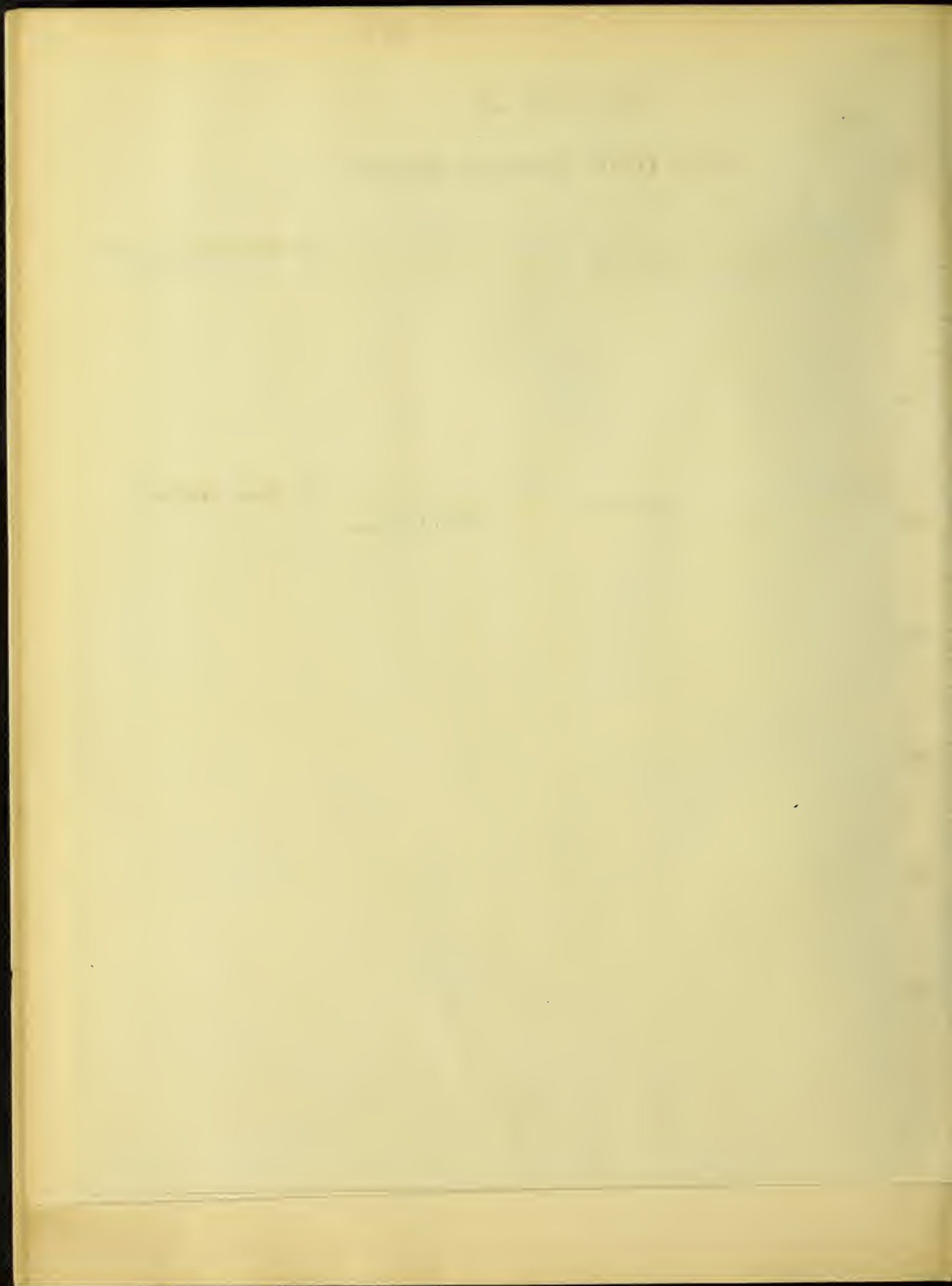


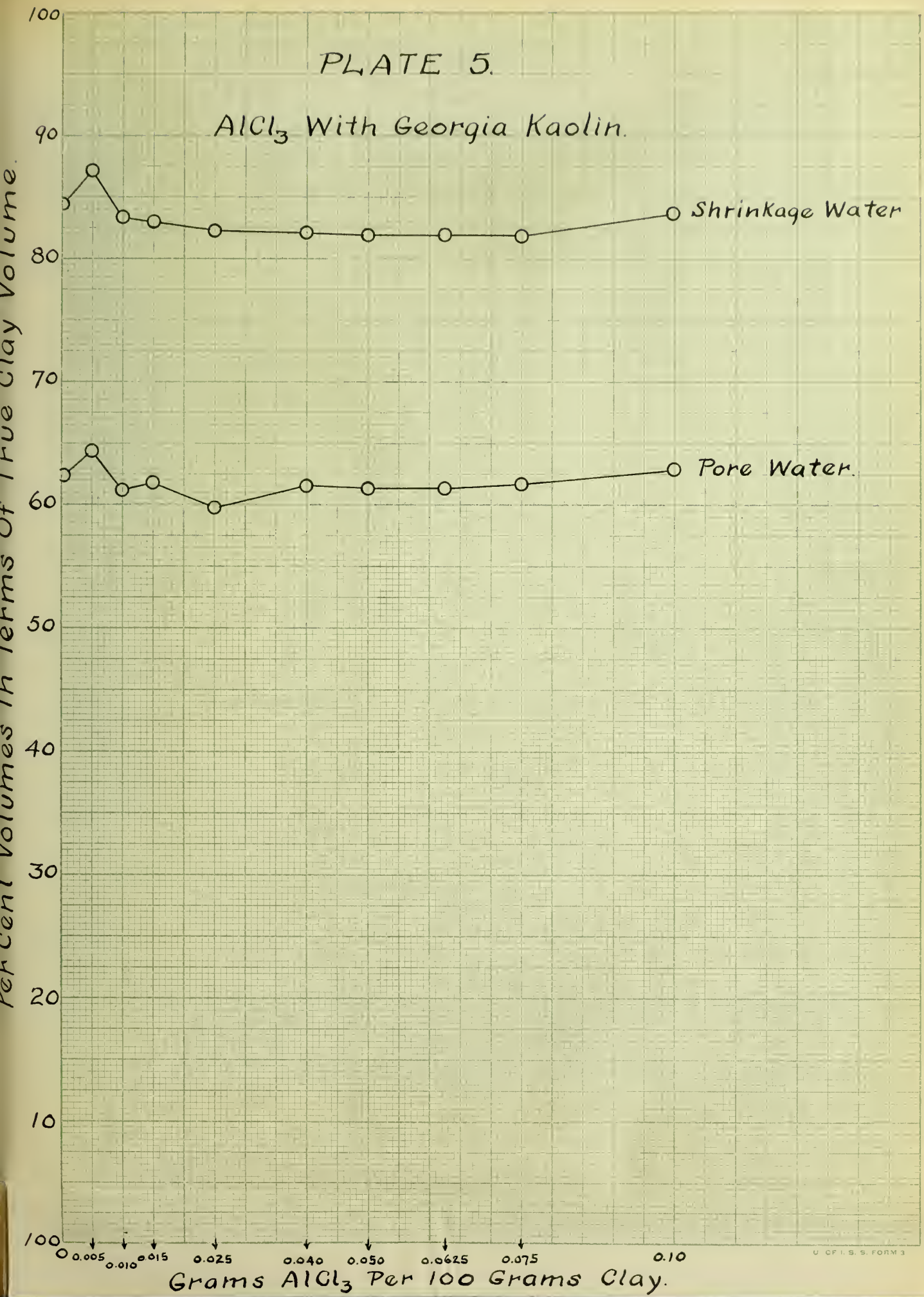


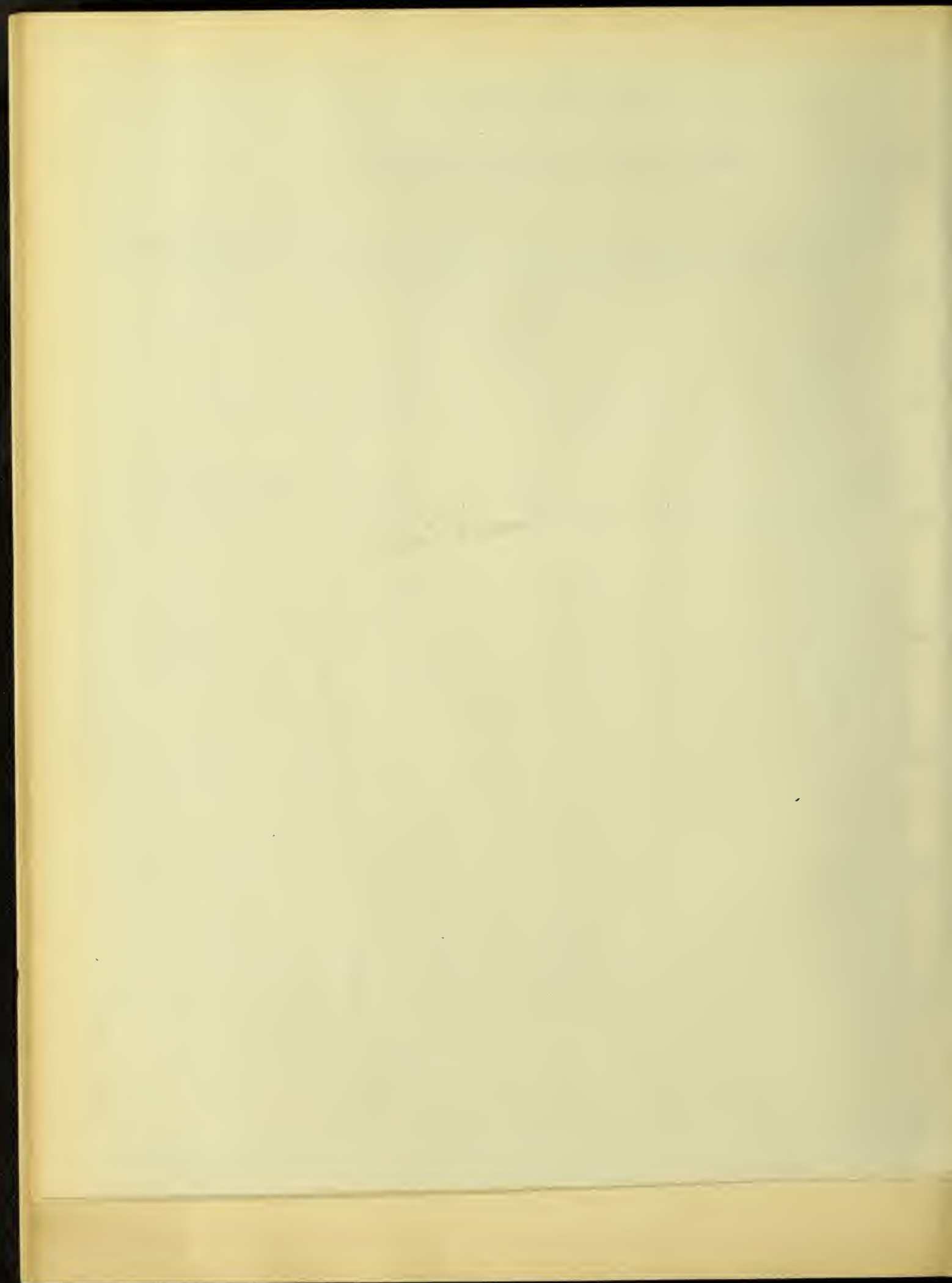
## PLATE 4.

 $\text{CaCl}_2$  With Georgia Kaolin.







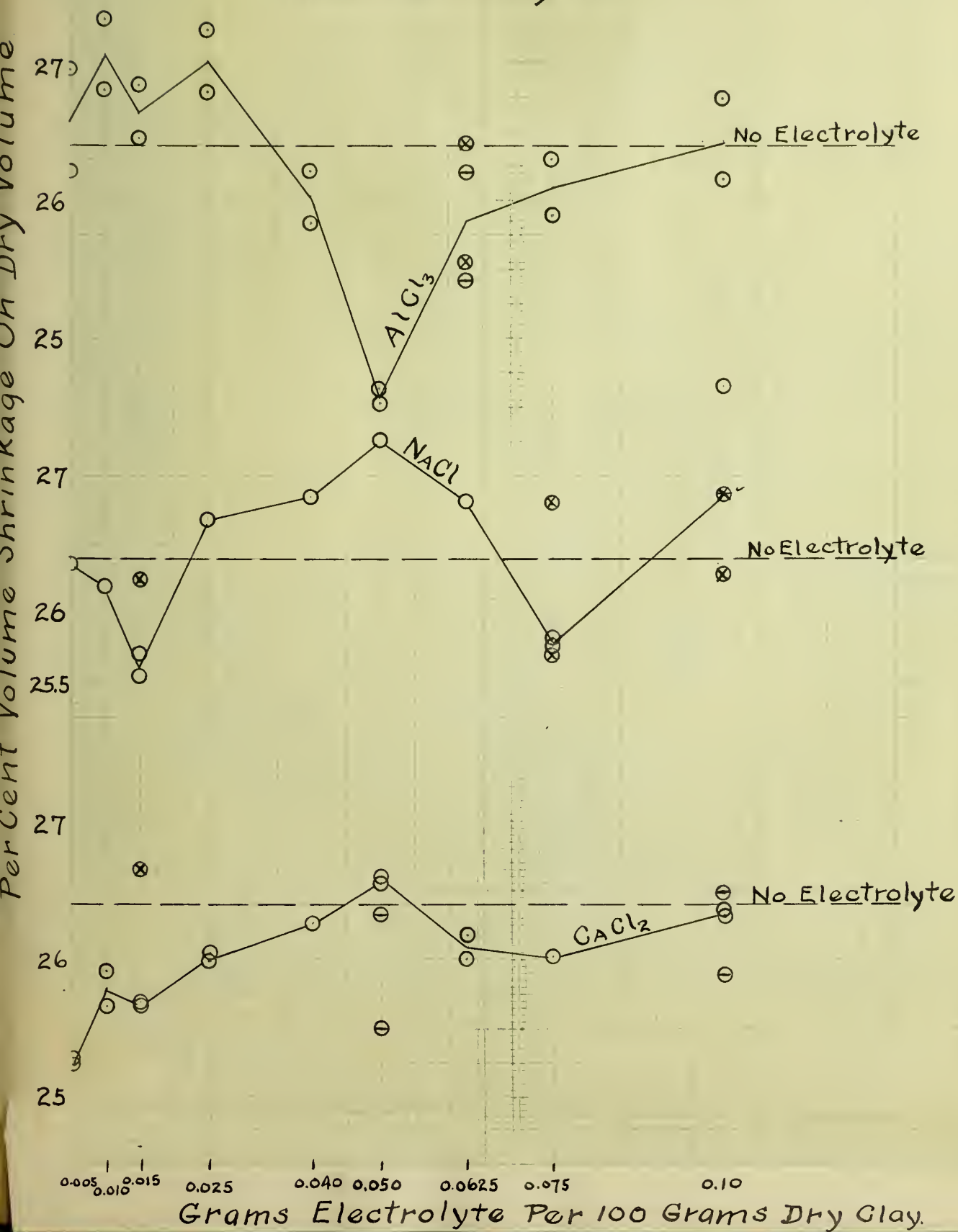


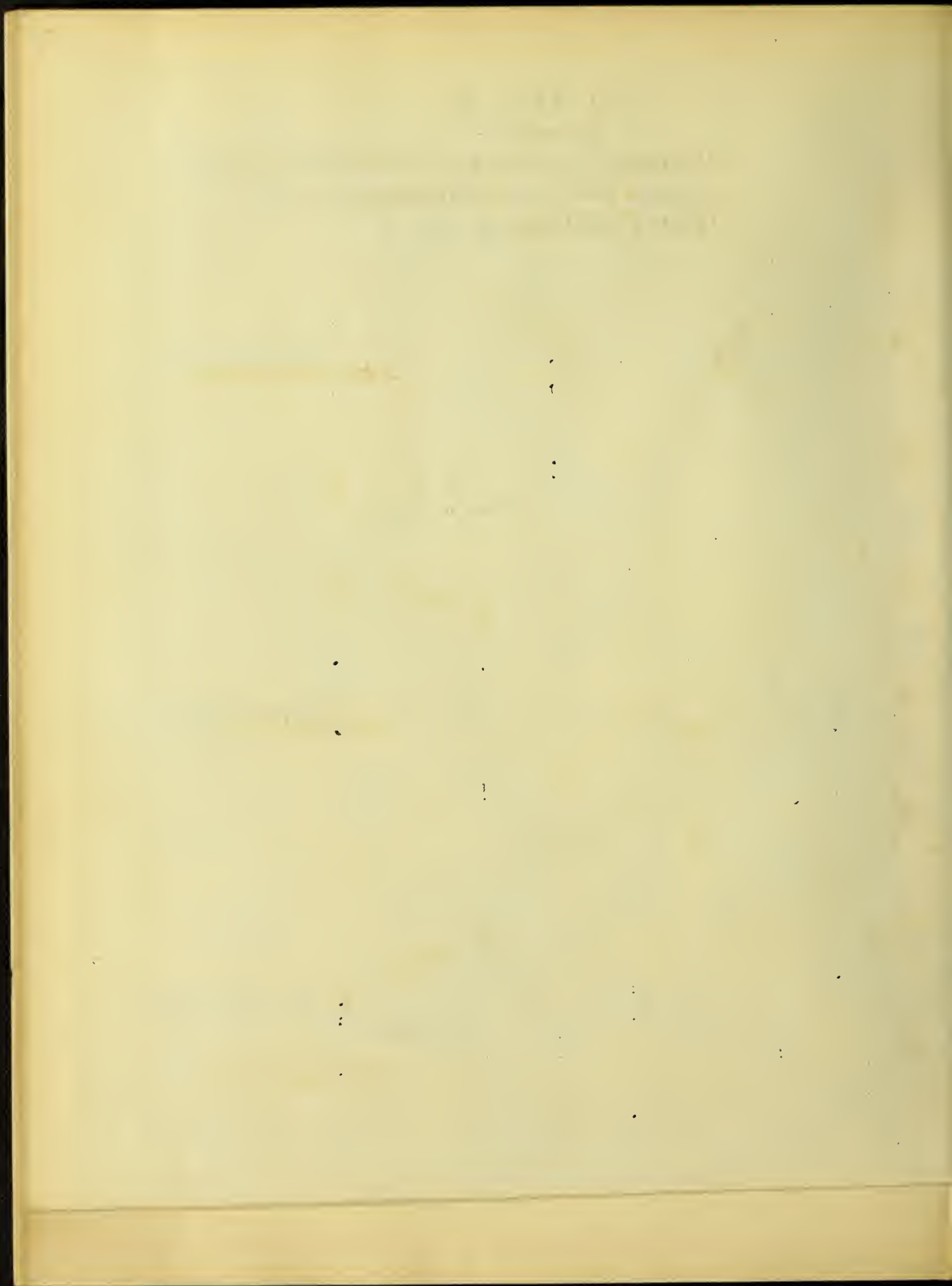


## PLATE 6.

## Curves

Showing Influence Of Electrolytes  
Upon Volume Shrinkage For  
Tenn. Ball Clay #I.



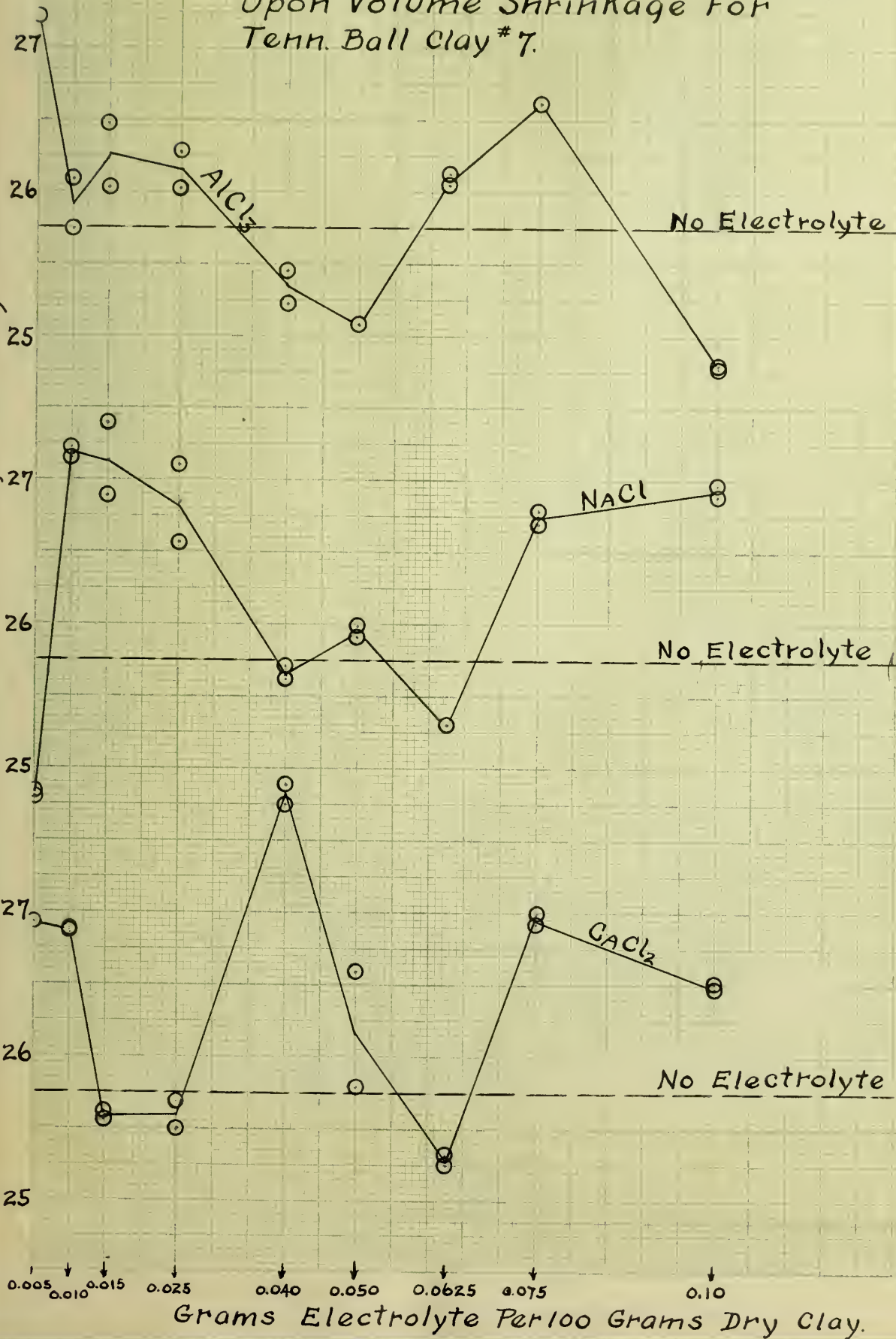


## PLATE 7.

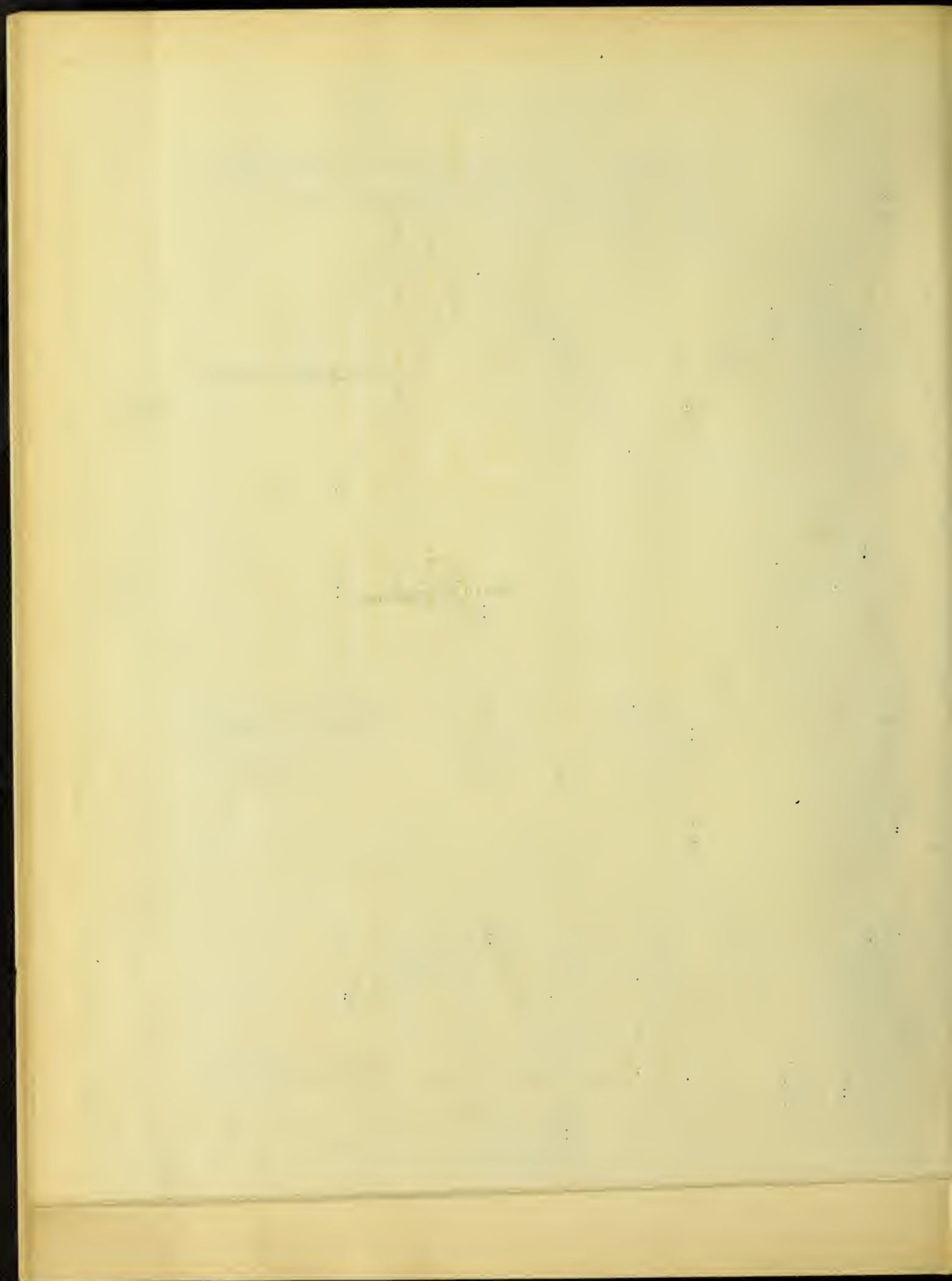
## Curves

Showing Influence Of Electrolytes  
Upon Volume Shrinkage For  
Tenn. Ball Clay #7.

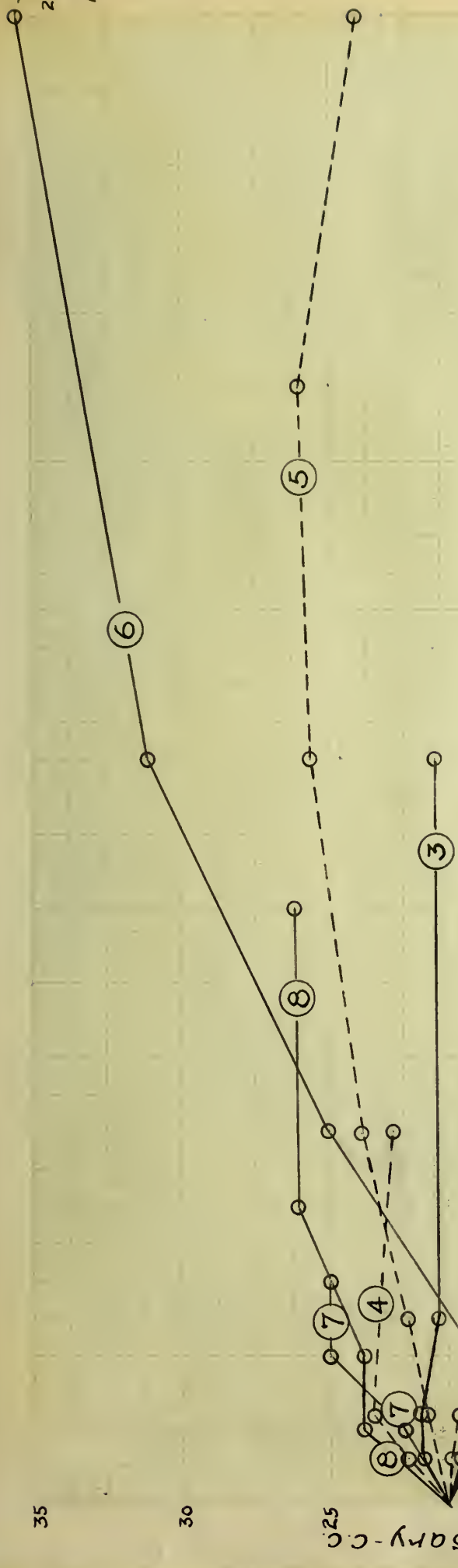
Per Cent Volume Shrinkage On Dry Volume.







27.12  
at  
1.5%



# PLATE 8

Curves showing effects of electrolytes in varying the volume of water needed to change 25 grams of clay paste to fluid condition so that it will just drop from a funnel, drop by drop, every 10 to 15 seconds.

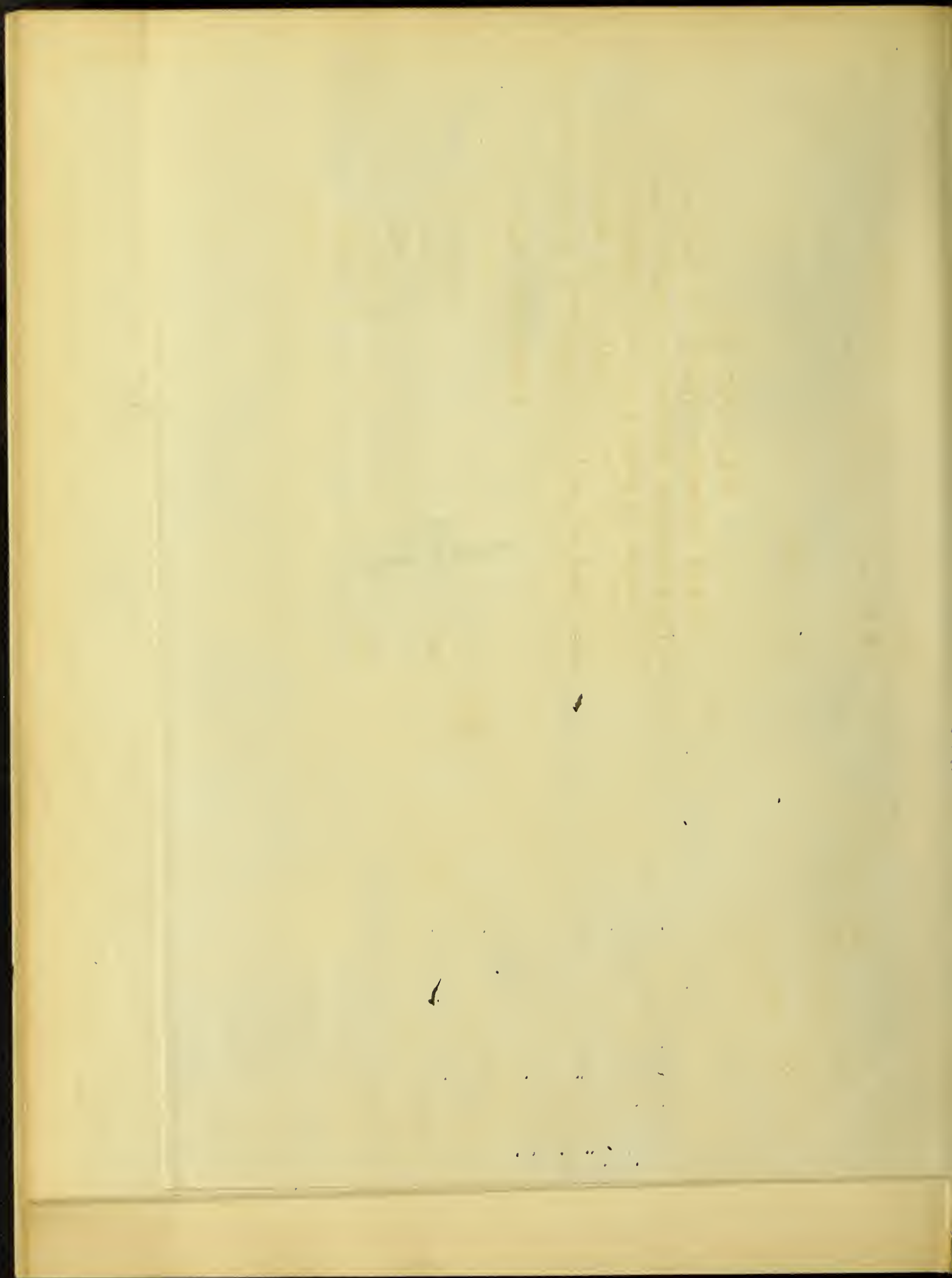
Georgia Kaolin

1.  $\text{Na}_2\text{SiO}_3$
2.  $\text{Na}_2\text{CO}_3$
3.  $\text{NaCl}$
4.  $\text{CaCl}_2$
5.  $\text{AlCl}_3$
6.  $\text{NaOH}$
7.  $\text{Ca(OH)}_2$
8.  $\text{Ba(OH)}_2$

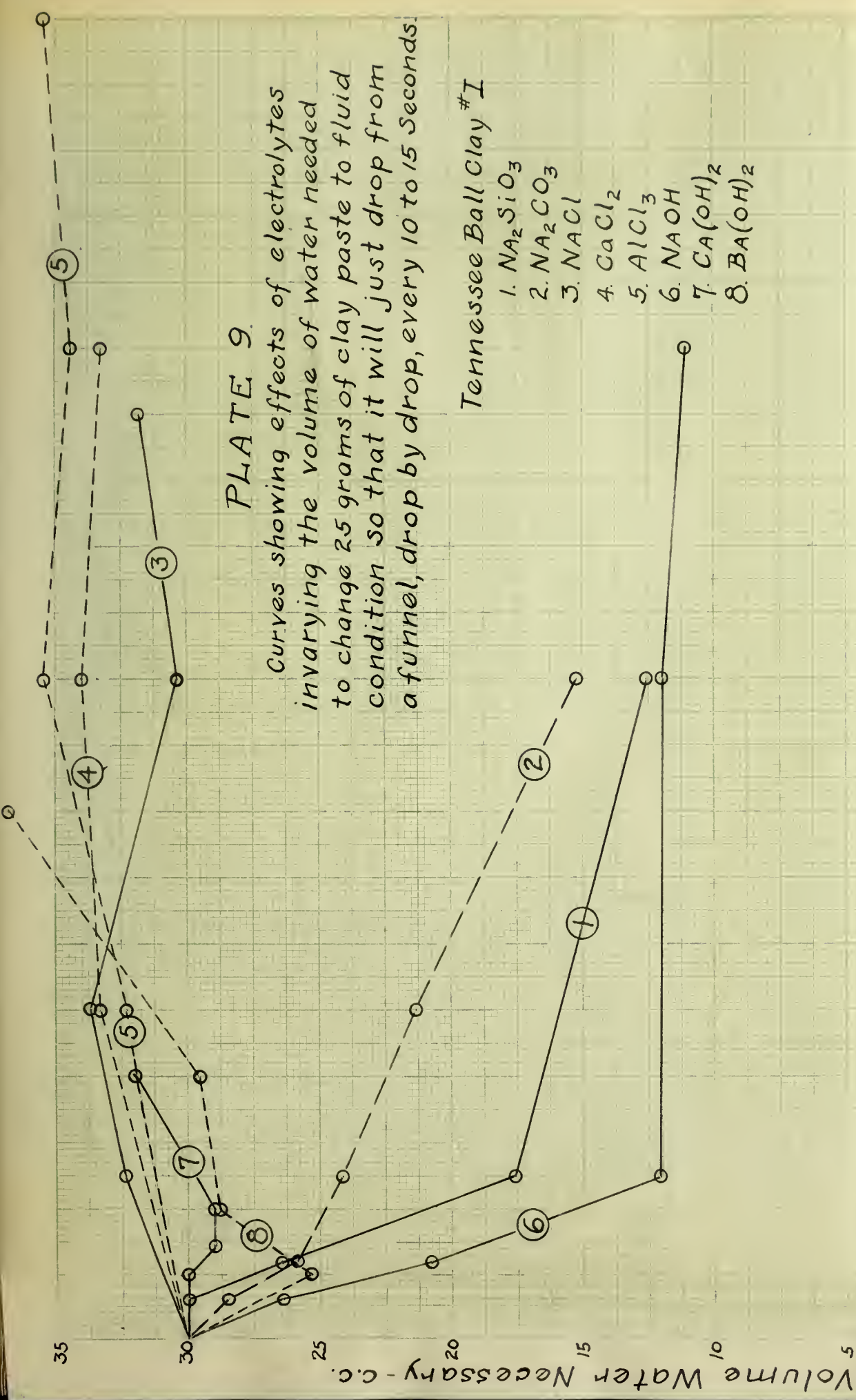
0 0.025 0.10 0.20 0.30 0.40 0.50 0.60 0.70 0.80 0.90 1.00

Per Cent Electrolytes On Weight of Clay (dried  $3\frac{1}{2}$  hours at  $110^\circ\text{C}$ )

17-F 100





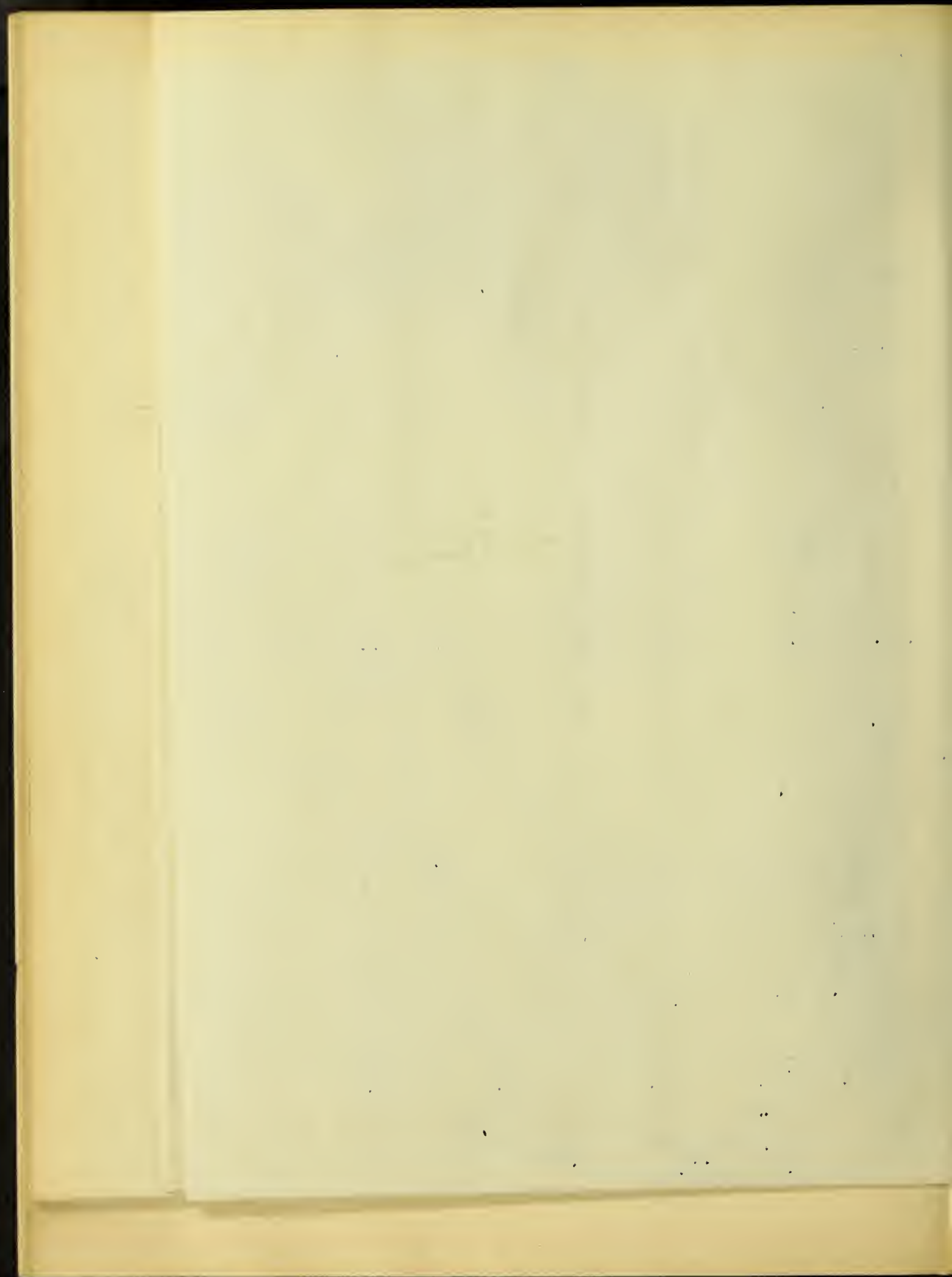


# PLATE 9

Curves showing effects of electrolytes  
 in varying the volume of water needed  
 to change 25 grams of clay paste to fluid  
 condition so that it will just drop from  
 a funnel, drop by drop, every 10 to 15 Seconds.

Tennessee Ball Clay #I

1.  $\text{Na}_2\text{SiO}_3$
2.  $\text{Na}_2\text{CO}_3$
3.  $\text{NaCl}$
4.  $\text{CaCl}_2$
5.  $\text{AlCl}_3$
6.  $\text{NaOH}$
7.  $\text{Ca}(\text{OH})_2$
8.  $\text{Ba}(\text{OH})_2$





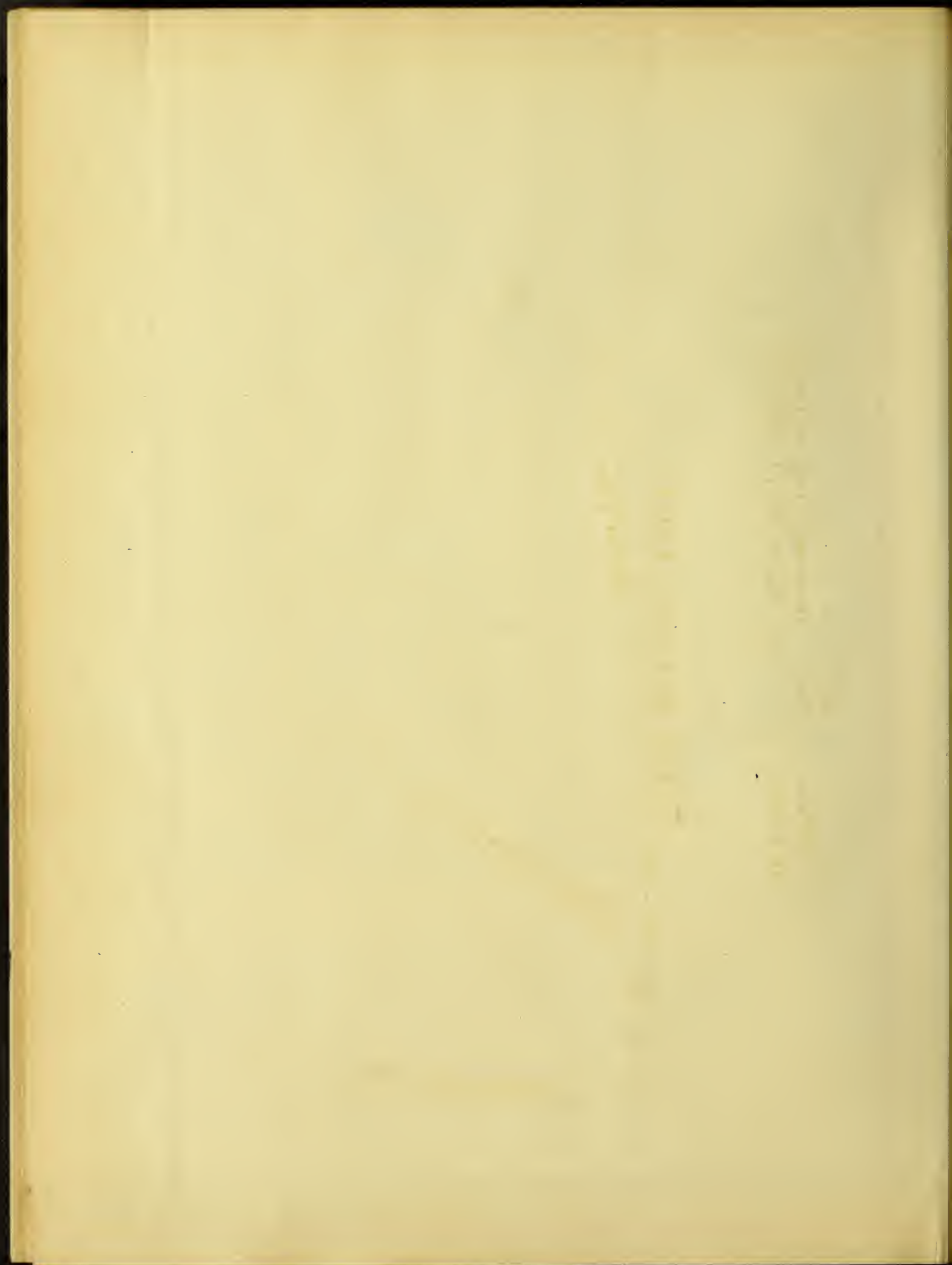
the variation in water content necessary with different concentrations of electrolytes to just make clay pastes of Georgia Kaolin and Tenn. Ball clay #1 respectively, flow from a small funnel, drop by drop, every 10 to 15 seconds. The funnel had a 2 inch stem of about 4 m.m. bore. Those concentrations of electrolytes were used which showed marked changes or maximum and minimum points in the curves plotted for the viscosity work with the mariotte tube. With Georgia kaolin,  $\text{Na}_2\text{SiO}_3$  and  $\text{Na}_2\text{CO}_3$  in small concentrations had the strongest influence in cutting down the quantity of water needed while  $\text{NaOH}$  showed an effect similar to that which it did in the viscosity measurement work with Georgia Kaolin as shown on plate #19. The  $\text{Na}_2\text{CO}_3$  and  $\text{Na}_2\text{SiO}_3$  additions produced a very syrupy and sticky mass that would easily flow from the funnel. With Tenn. Ball clay #1,  $\text{Na}_2\text{SiO}_3$ ,  $\text{Na}_2\text{CO}_3$  and  $\text{NaOH}$  in small concentrations had the strongest effect in cutting down the water needed.  $\text{Ca}(\text{OH})_2$  and  $\text{Ba}(\text{OH})_2$  in 0.05 to 0.10 per cents also cut down the water needed to a smaller extent. These results are given graphically on plate #9.

The influence of these electrolytes upon surface tension of the liquid medium and corresponding flocculating and deflocculating effects upon clays, are used to explain the work as represented on plates #8 and #9.

#### IV. The Flocculation of Dilute Clay Solutions.

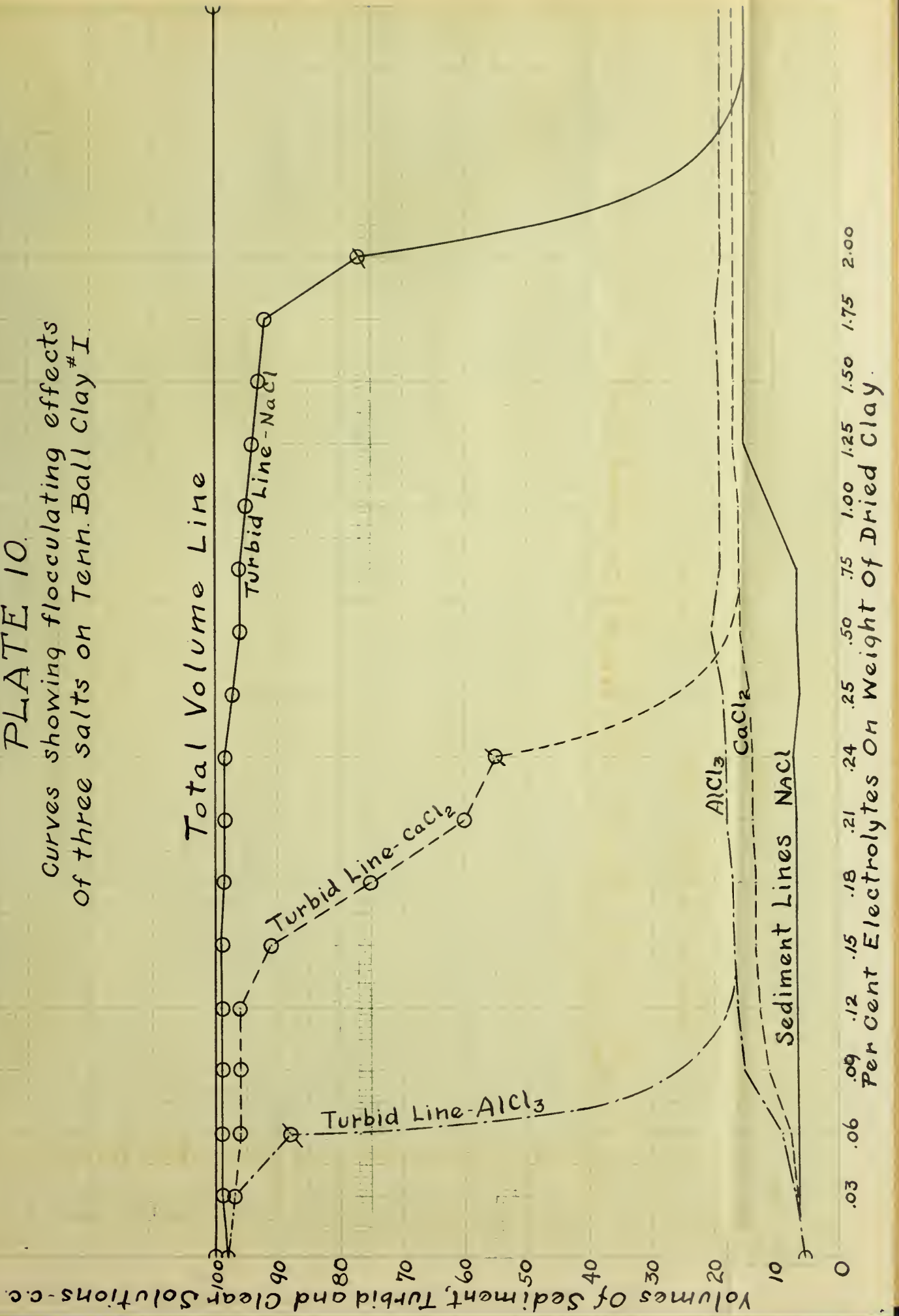
The flocculating effects of the three chlorides upon Tenn. Ball clay #1 and Georgia Kaolin in dilute solution ( 5 grams dried clay per 100 c.c. solution) are shown graphically on plates #10 and #11 respectively. The effects are self evident from these plates and it is observed that the coagulating power of these salts is in the order of their valency. Also the speed of coagulation for  $\text{CaCl}_2$

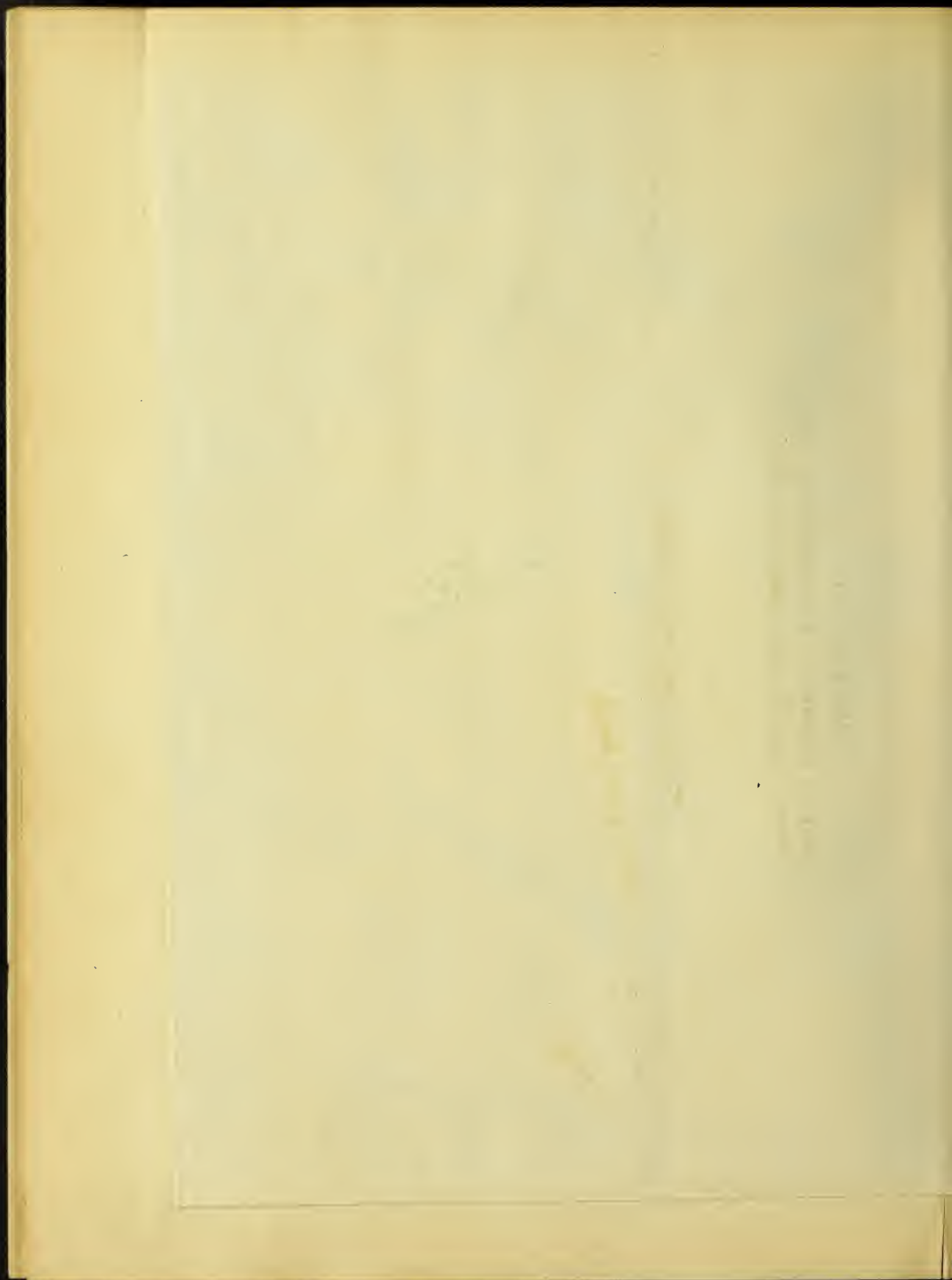




# PLATE 10.

Curves showing flocculating effects  
of three salts on Tenn. Ball Clay #I.

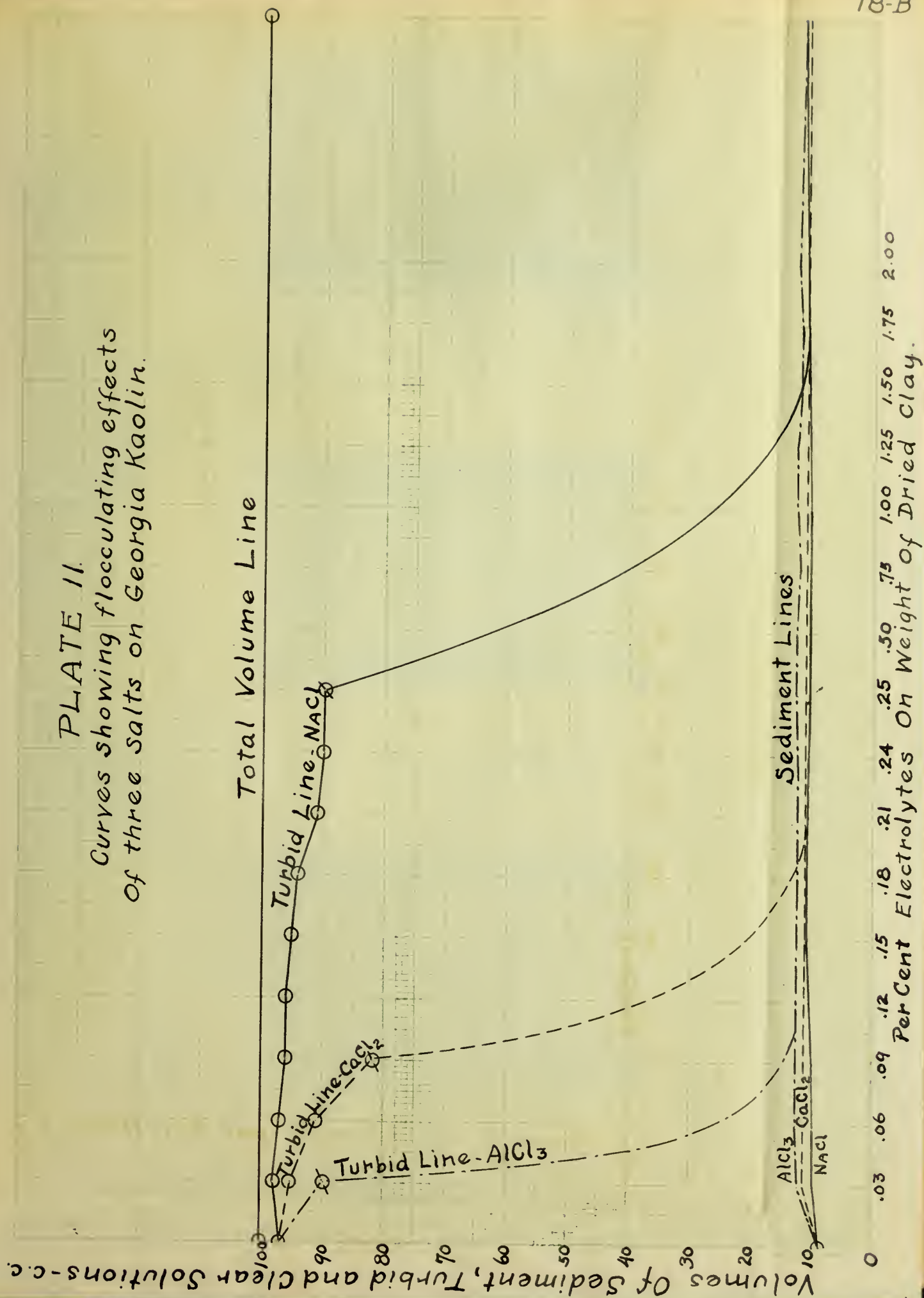






## PLATE II.

Curves showing flocculating effects  
of three salts on Georgia Kaolin.





I.



0.0 .03 .06 .09 .12 .15 .18 .21 .24

PerCent NaCl.

2



0.0 .03 .06 .09 .12 .15 .18 .21 .24

PerCent  $\text{CaCl}_2$ 

3.



0.0 .03 .06 .09 .12 .15 .18 .21 .24

PerCent  $\text{AlCl}_3$ 

The Flocculation Of  
Georgia Kaolin.





4-a



0.0 .03 .06 .09 .12 .15 .18 .21 .24

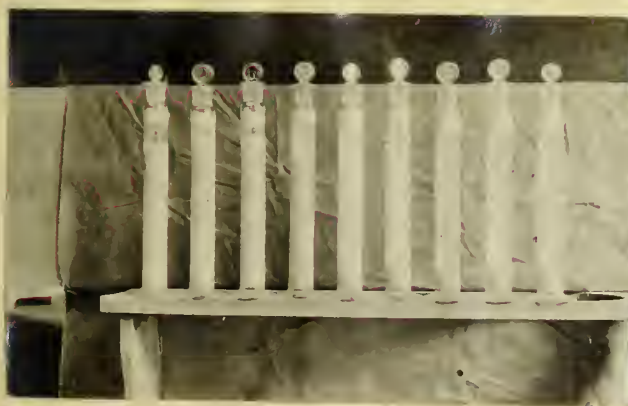
4-b



0.0 .25 .50 .75 1.00 1.25 1.50 1.75 2.00

Per Cent  $\text{NaCl}$ 

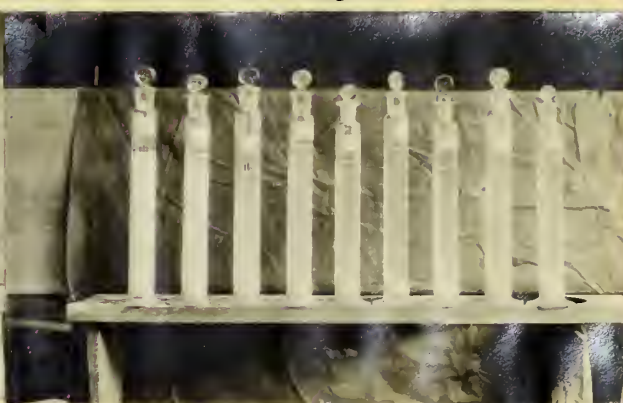
5.



0.0 .03 .06 .09 .12 .15 .18 .21 .24

Per Cent  $\text{CaCl}_2$ 

6.



0.0 .03 .06 .09 .12 .15 .18 .21 .24

Per Cent  $\text{AlCl}_3$ 

The Flocculation Of  
Tennessee Ball Clay #I.





and  $\text{AlCl}_3$  was greater than that for the  $\text{NaCl}$ . Photographic prints No. 1 to 3 are for  $\text{NaCl}$ ,  $\text{CaCl}_2$  and  $\text{AlCl}_3$  with Georgia kaolin and No. 4a, 4b, 5 and 6 are for these salts with Tenn. Ball clay #1.

#### V. Mechanical Analyses and Malachite Green Absorptions.

Mechanical analyses of both Georgia kaolin and Tenn. Ball clay #1 were made with the Schoene Elutriating apparatus after first deflocculating the 5 gram samples of clay with sodium hydroxide solution. From the results of the analyses, the total surface factors were calculated and found to be 61.57 and 40.94 for Tenn. Ball clay #1 and Georgia kaolin respectively. The ratio is approximately 3 to 2. This coincides quite closely to the ratio of relative colloids between these two clays as determined by the malachite green adsorption test in which the relative colloid values were found to be 66 and 39.23 for Tenn. Ball Clay #1 and Georgia Kaolin respectively. Using this data to calculate plasticity values by Ashley's formula we get the following results;-

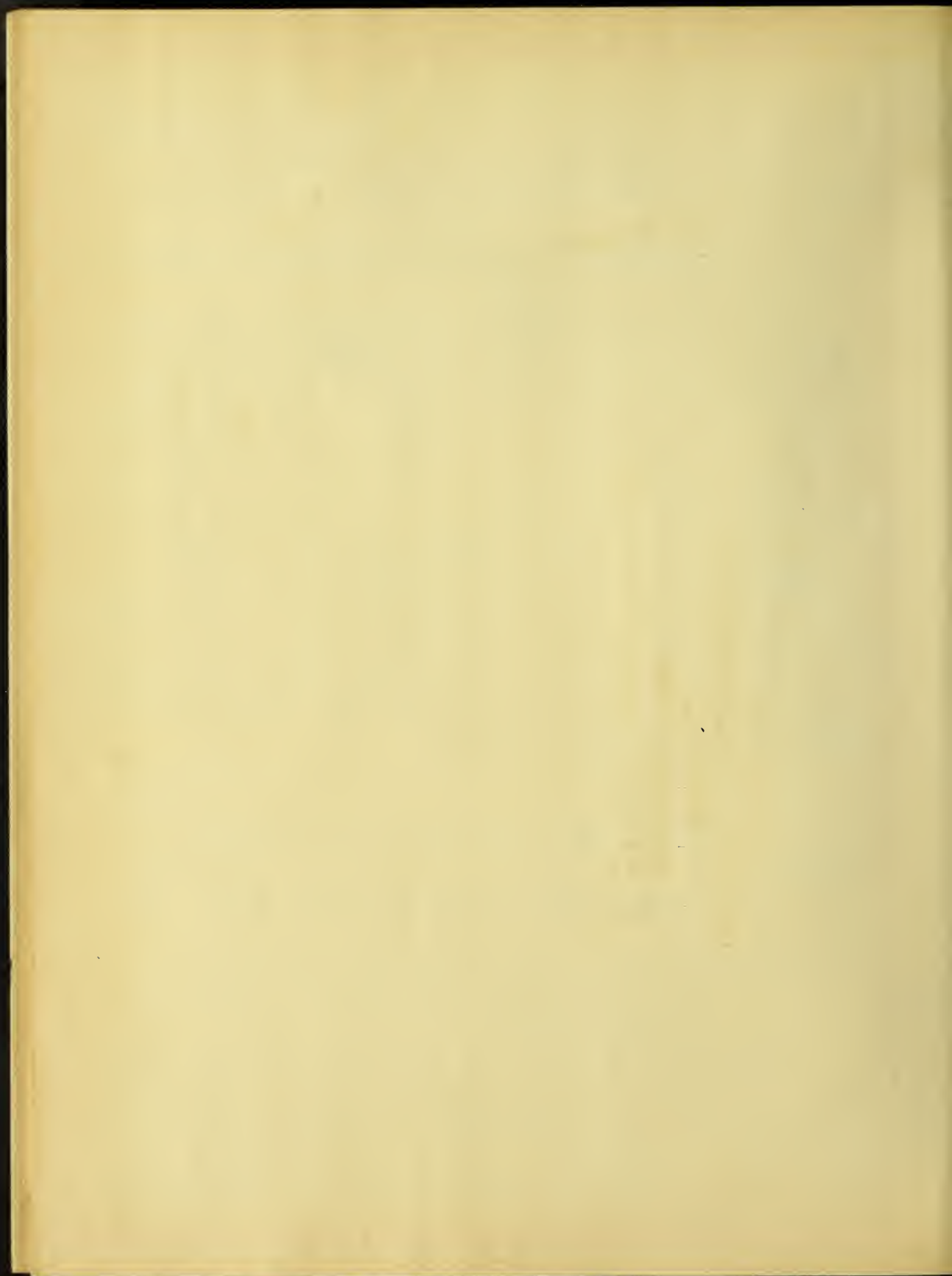
$$G = \frac{c \times B}{A}$$

$$G = \frac{66 \times 31.6}{61} = 34.2 \text{ for Tenn. Ball Clay \#1}$$

$$G = \frac{39.23 \times 15.2}{41} = 14.55 \text{ for Georgia Kaolin.}$$

#### VI. Viscosity Measurements of Clay Slips and Determinations of Possible Errors.

The effect of electrolytes on Tenn. Ball clay #1 and Georgia Kaolin in the state of slip consistency was studied by making viscosity measurements with a modification of the mariotte tube as shown in Fig. I. Plate #12, shows the results of experiments made



# PLATE 12. Viscosity Of Clay Solutions with the

Mariotte Tube

A' = A plus  $\frac{1}{4}\%$   $Na_2SiO_3$  plus 30 c.c.  $H_2O$

B' = B " " " " " "

Time of Flow - Seconds

15

30

45

60

75

19-A

Grams Clay Per 100 c.c. Water.

over 30m

Tenn. Ball Clay #1

Georgia Kaolin

X

Y

B'

A'

B

A



1. 1. 1.

1. 1. 1.

1. 1. 1.

1. 1. 1.

1. 1. 1.

to determine the proportion of dried clay and water to use for a slip of the consistency used in casting. Fifty grams of dried clay with 100 c.c. distilled water was selected as a standard slip.

When the clay was increased from 60 to 75 grams per 100 c.c. of water, the solutions became very viscous as shown by the curves of plate #12. Adding thirty c.c. of water reduces the viscosity as shown by points "X" and "Y". Adding 1 per cent by weight of  $\text{Na}_2\text{SiO}_3$  to the diluted slips, points A' and B' are obtained. Clay samples were dried only one hour at  $110^\circ\text{C}$  for work represented by plate #12 except for points "X" and "Y" clay was heated  $3\frac{1}{2}$  hours to bring these points down as low as possible for water alone.

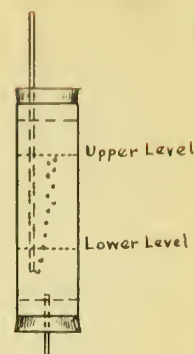
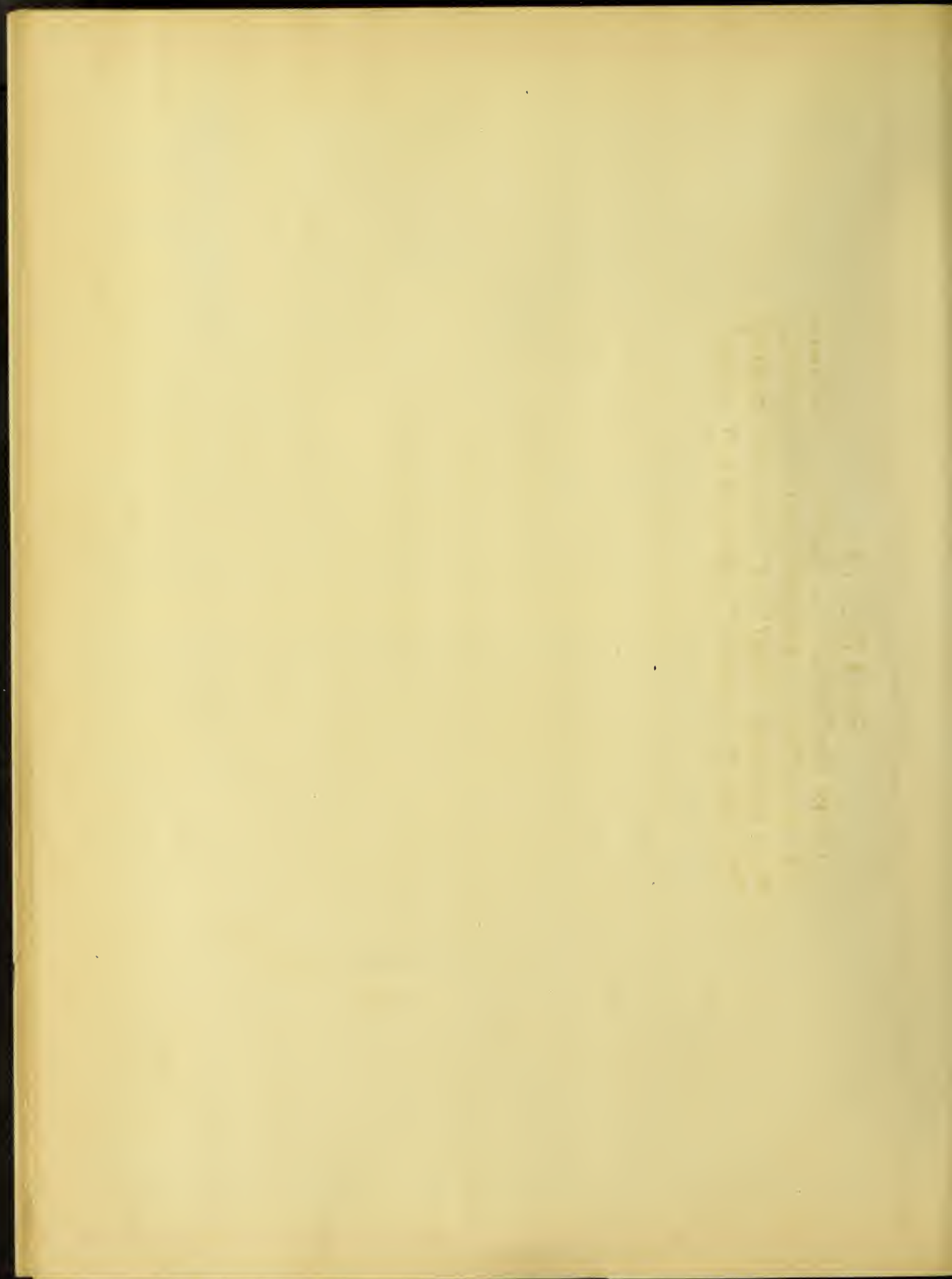


Fig. I.

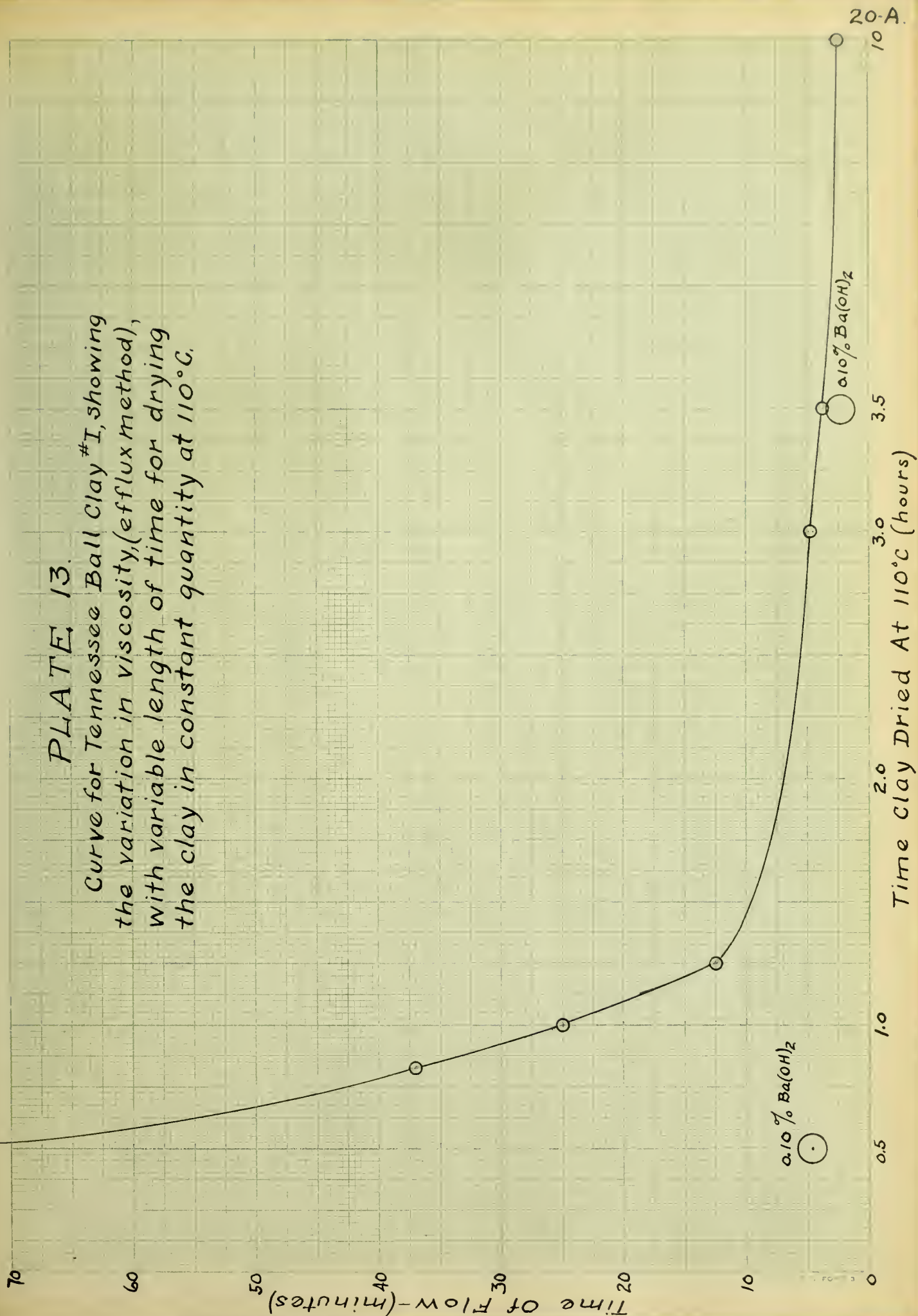
Plates #13, 14, and 15 represent the results of experiments performed to determine the probable error in viscosity determinations. Plate #13 shows that the clay samples must be dried at least  $3\frac{1}{2}$  hours at  $110^\circ\text{C}$  in order to have a slip of uniform viscosity for all tests with electrolytes. From plate #13, it is very apparent that the colloidal structure of the clay is much affected by drying at  $110^\circ\text{C}$ , the colloids probably being partially changed to a set or less active condition, that of collected molecules or gel formation, in which the more soluble portions of colloid content are not so readily dissociable. Hence the colloid-gels do not readily increase the viscosity of the liquifying medium and thereby give a much lower value for viscosity than is obtained with clay heated for shorter periods. It cannot be due to the driving off of mechanical water alone for in that case the thoroughly dried clay should then require much more water to obtain the same low



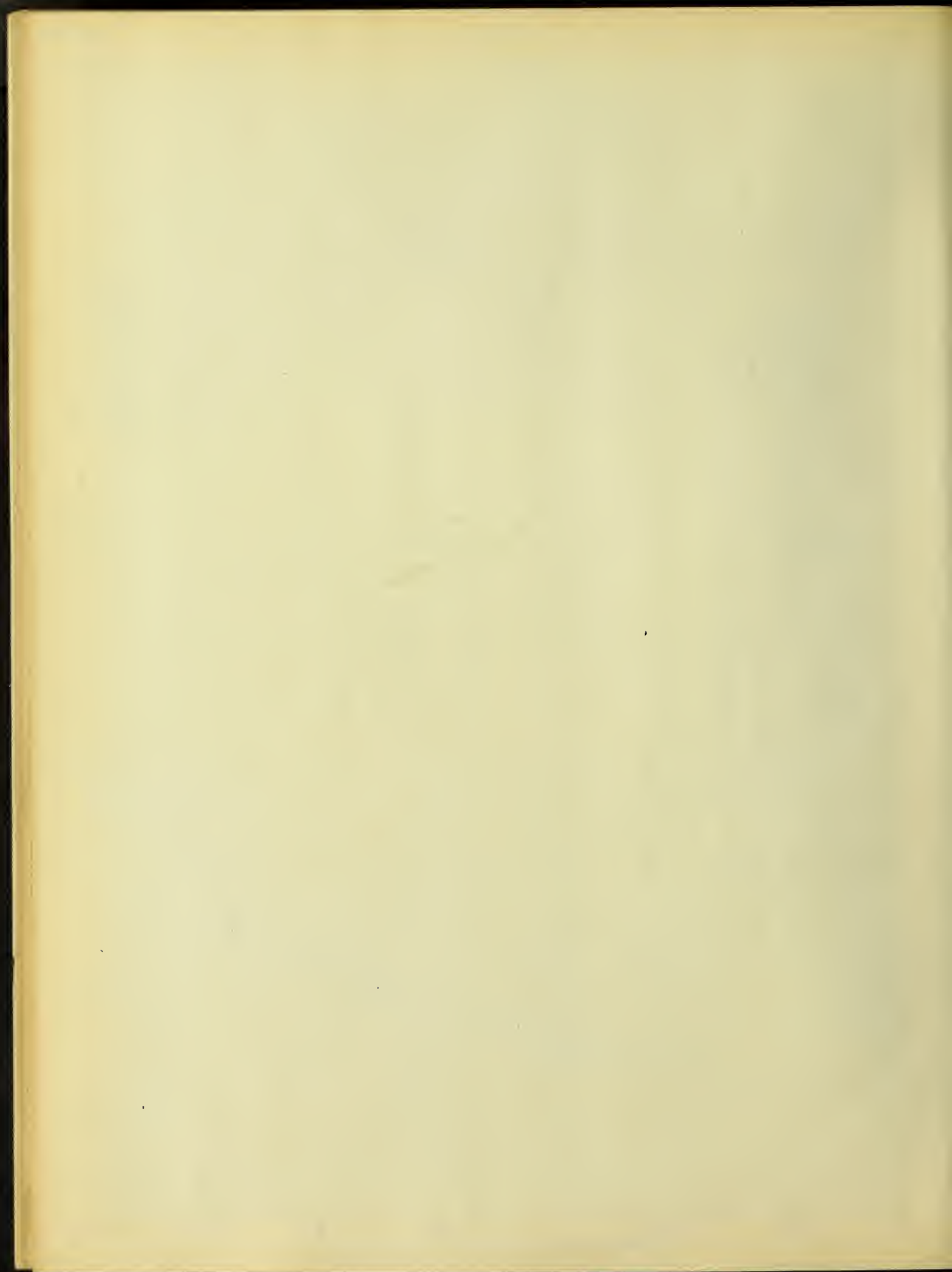


# PLATE 13.

Curve for Tennessee Ball Clay #1, showing the variation in viscosity, (efflux method), with variable length of time for drying the clay in constant quantity at 110°C.



20-A.



Variable Temperature Curve

Effect of variable temperature not appreciable.

Variable Water Curve

2% H<sub>2</sub>O increase effects viscosity by 4.08%  
 4% " " " " 9.18%  
 9% " " " " 28.57%  
 Work performed within 1.0% H<sub>2</sub>O variation.

Curve For Variable Time of Standing  
 10% change of viscosity in 1 hour

Minutes Slip Had Been Made Before Tested.

# PLATE 14.

Curves showing possibility of introducing error in viscosity measurements of clay slip using the Mariotte tube.

Clay used - Tenn. Ball #I

Used efflux tube - 6mm. diam.



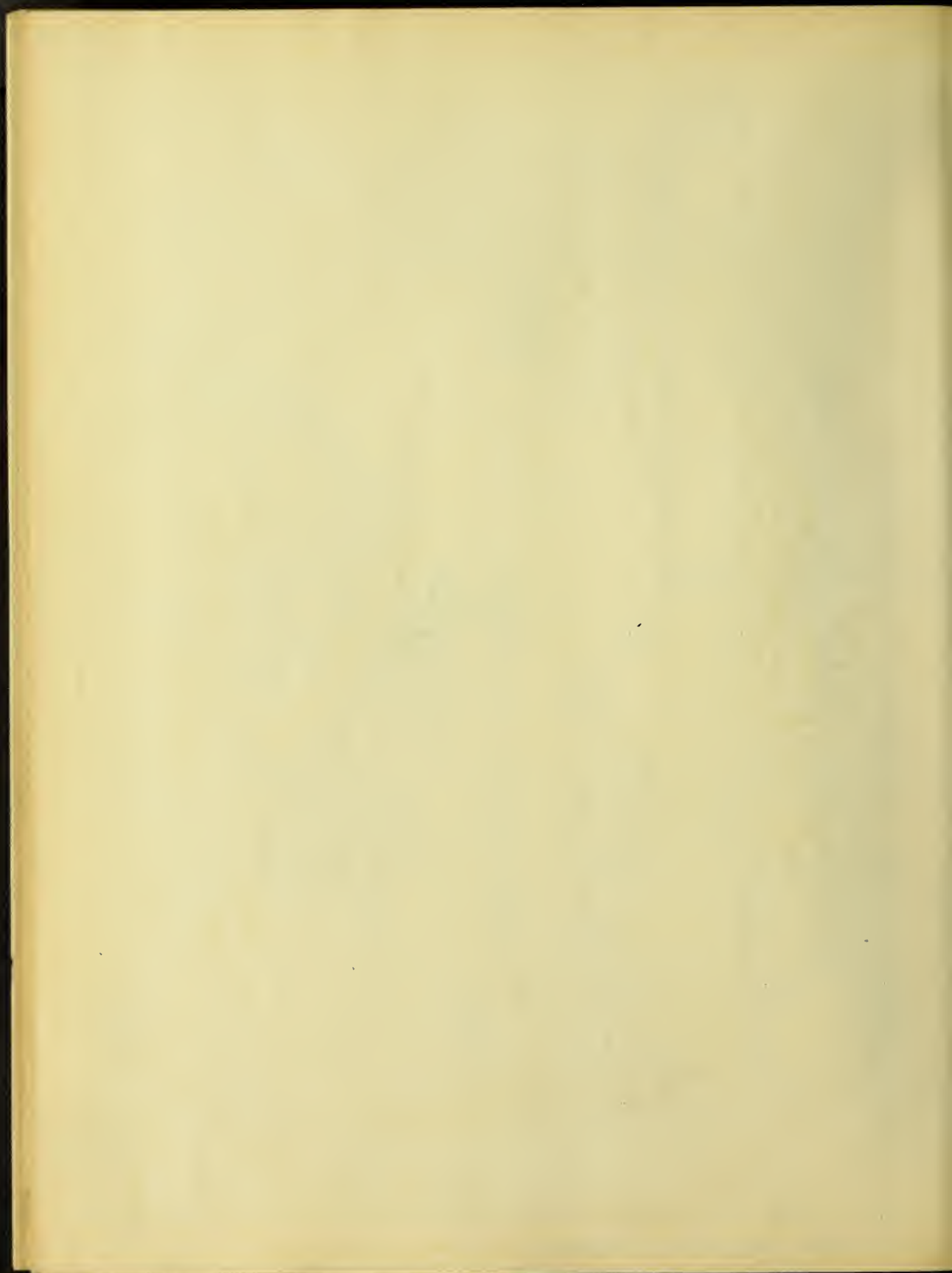
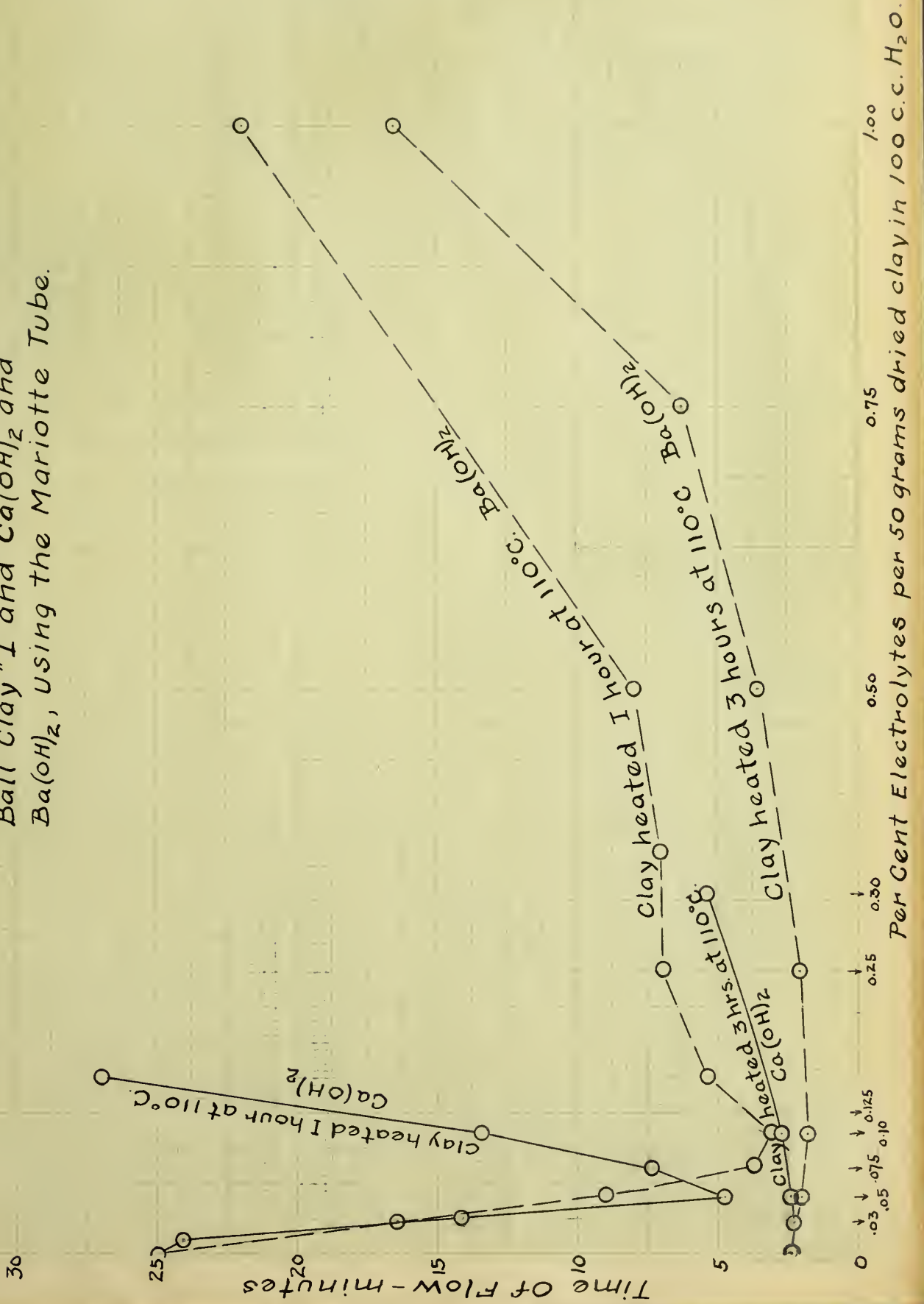
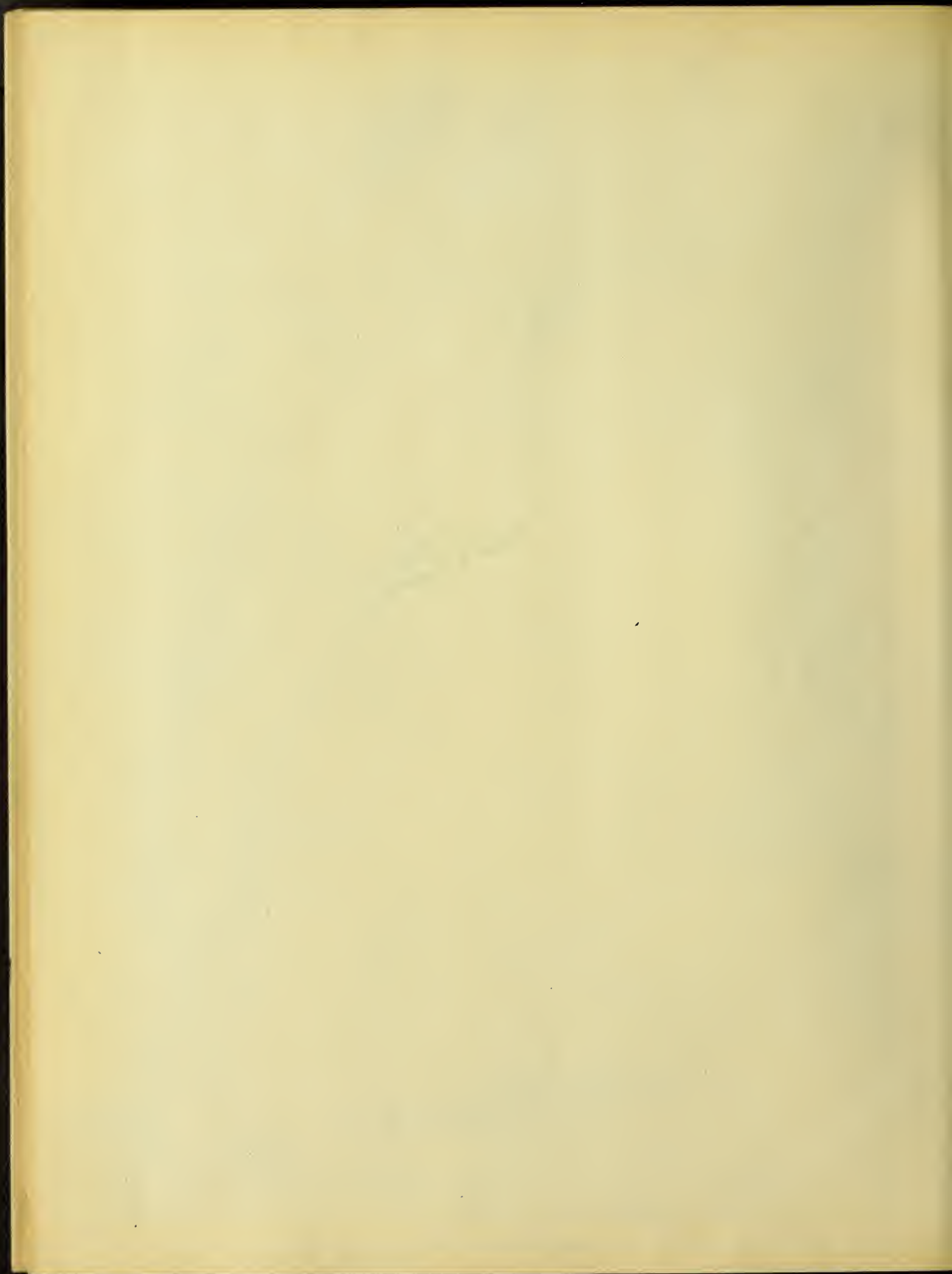


PLATE 15.  
Viscosity Tests For Tenn.  
Ball Clay #I and  $\text{Ca}(\text{OH})_2$  and  
 $\text{Ba}(\text{OH})_2$ , Using the Mariotte Tube.

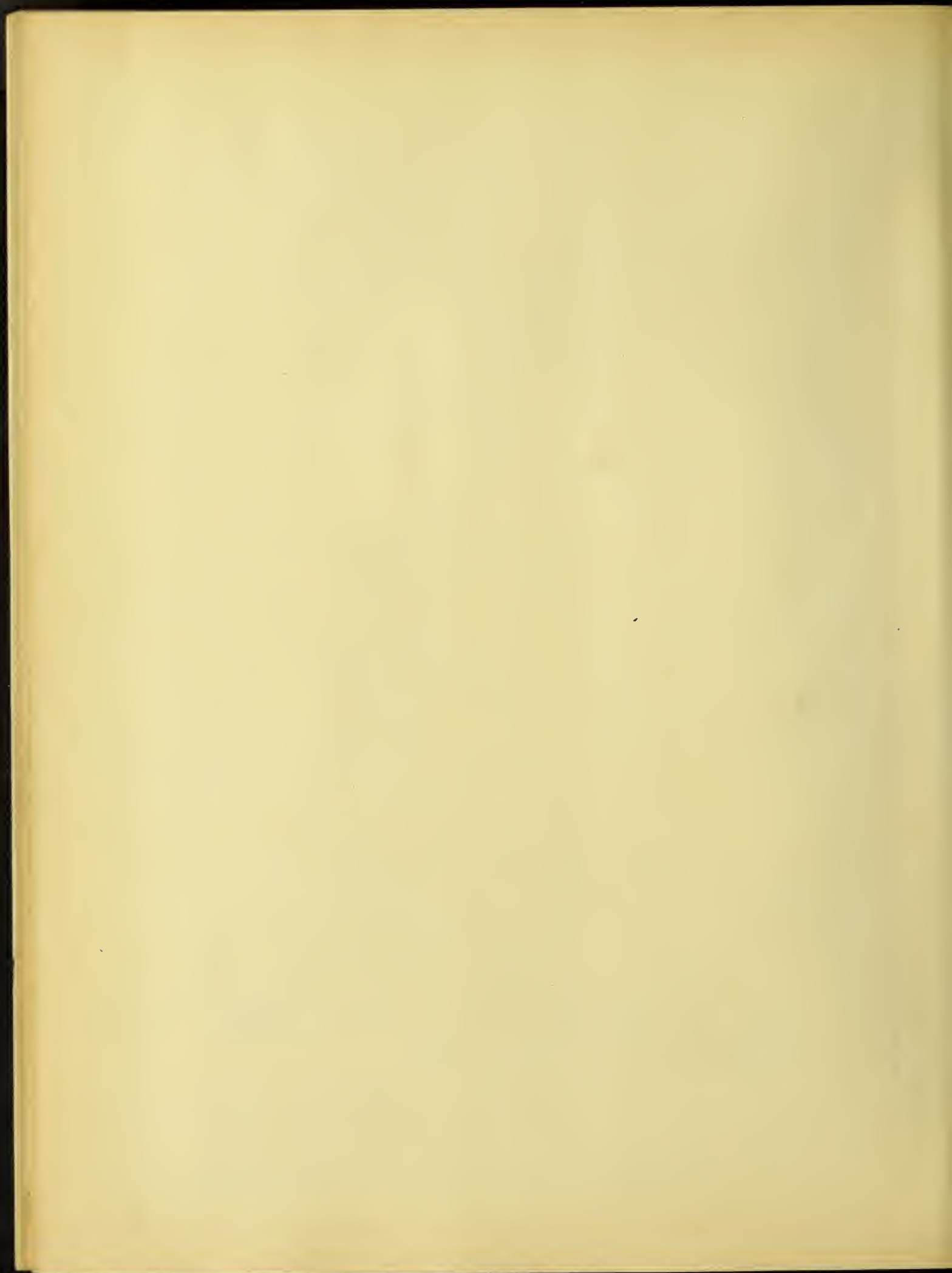






viscosity. But the viscosity is found to be lower with the same water content. The colloid structure must have been partially set. The large circles on plate #13 show that 0.10%  $\text{Ba(OH)}_2$  lowers the time of flow for a given quantity of slip down to 4½ minutes for clay heated only ½ hour at  $110^\circ\text{C}$ ., while the time is 2½ minutes for clay heated 3½ hours. Plate #14 shows curves, illustrating, separately, the error due to variable temperature, variable quantities of water and variable time of standing of the slips. Any error due to temperature variation was not noticeable in amount. Water variation gives rise to considerable error but all the tests were made within 1% water variation which would only affect the viscosity measurement by about  $\pm 2\%$ . For clay dried only one or two hours at  $110^\circ\text{C}$ ., a considerable error is introduced by allowing a slip to stand an hour or longer before testing. The viscosity is noticeably increased by long standing. But if the clay is dried 3½ hours or more at  $110^\circ\text{C}$ ., the increase in viscosity due to standing in an air tight jar is hardly noticeable even after 24 hours when 0.50%  $\text{NaOH}$  is used as is illustrated on plate #22. But if distilled water alone is used in the latter case, the viscosity would be appreciably increased on long standing but not rapidly as with clay heated for a shorter period. However the final viscosity of the slip with clay heated for the longer period would most probably be the greater. The viscosity tests were made immediately after thoroughly mixing the slip and constant viscosity values were obtained for repeated tests.

Plate #15 shows the effect of  $\text{Ca(OH)}_2$  and  $\text{Ba(OH)}_2$  on Term. Ball Clay #1 slips with clay heated at  $110^\circ\text{C}$  for one and 3 hours respectively. This plate clearly shows how misleading data would



be obtained in viscosity measurements if constant quantities of clay samples were not dried at  $110^{\circ}\text{C}$  to a constant viscosity value with water alone before testing the effects of any electrolyte solutions with clay slips.

In all the following work on viscosity tests with the mariotte tube, the quantity of drying clay was kept constant, the temperature was kept at  $110^{\circ}\text{C}$ , and the clay was dried at this temperature for three or more hours until the approximately constant time value of 2' 15" to 2' 30" for the efflux of a constant quantity, by volume of a slip was obtained.

#### VII. Viscosities of Clay Slips, Using Electrolytes.

Plate #16 illustrates the effects which  $\text{NaCl}$ ,  $\text{CaCl}_2$ , and  $\text{AlCl}_3$  have upon the viscosity of Tenn. Ball Clay #1 slip. All, three salts, apparently act as flocculating agents and consequently increase the viscosity of the clay slip. The  $\text{AlCl}_3$  shows a marked increase in viscosity for the higher concentrations which can possibly be accounted for by the fact that  $\text{AlCl}_3$  is readily hydrolysed forming  $\text{HCl}$  and  $\text{Al}(\text{OH})_3$ . The  $\text{HCl}$  accelerates coagulation due to the content of  $\text{H}^+$ -ions. The  $\text{Al}(\text{OH})_3$  is possibly partly acted upon by alkali salts present in the clay to form soluble aluminates until equilibrium is obtained. For concentrations of  $\text{NaCl}$  and  $\text{CaCl}_2$  greater than 0.50%, the viscosity is lowered slightly. The effects of  $\text{NaCl}$ ,  $\text{CaCl}_2$ , and  $\text{AlCl}_3$  upon the viscosity of Georgia Kaolin slips are shown by plate #17. The viscosity is lowered slightly for the smallest concentration of those salts, somewhat in the order of their valencies but the flocculating influence of any of these salts is not manifested with Georgia Kaolin as it was with Tenn. Ball Clay. The time of flow is taken and



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# PLATE 16.

of  
Tenn. Ball Clay #1 Solutions (slips)  
with the  
MARIOTTE TUBE.

Time of Flow - Minutes.

90

75

60

45

30

15

U

OF

S.

FORM 3

0

$\text{CaCl}_2$

$\text{AlCl}_3$

$\text{NaCl}$

.0625 0.125 0.25

.50

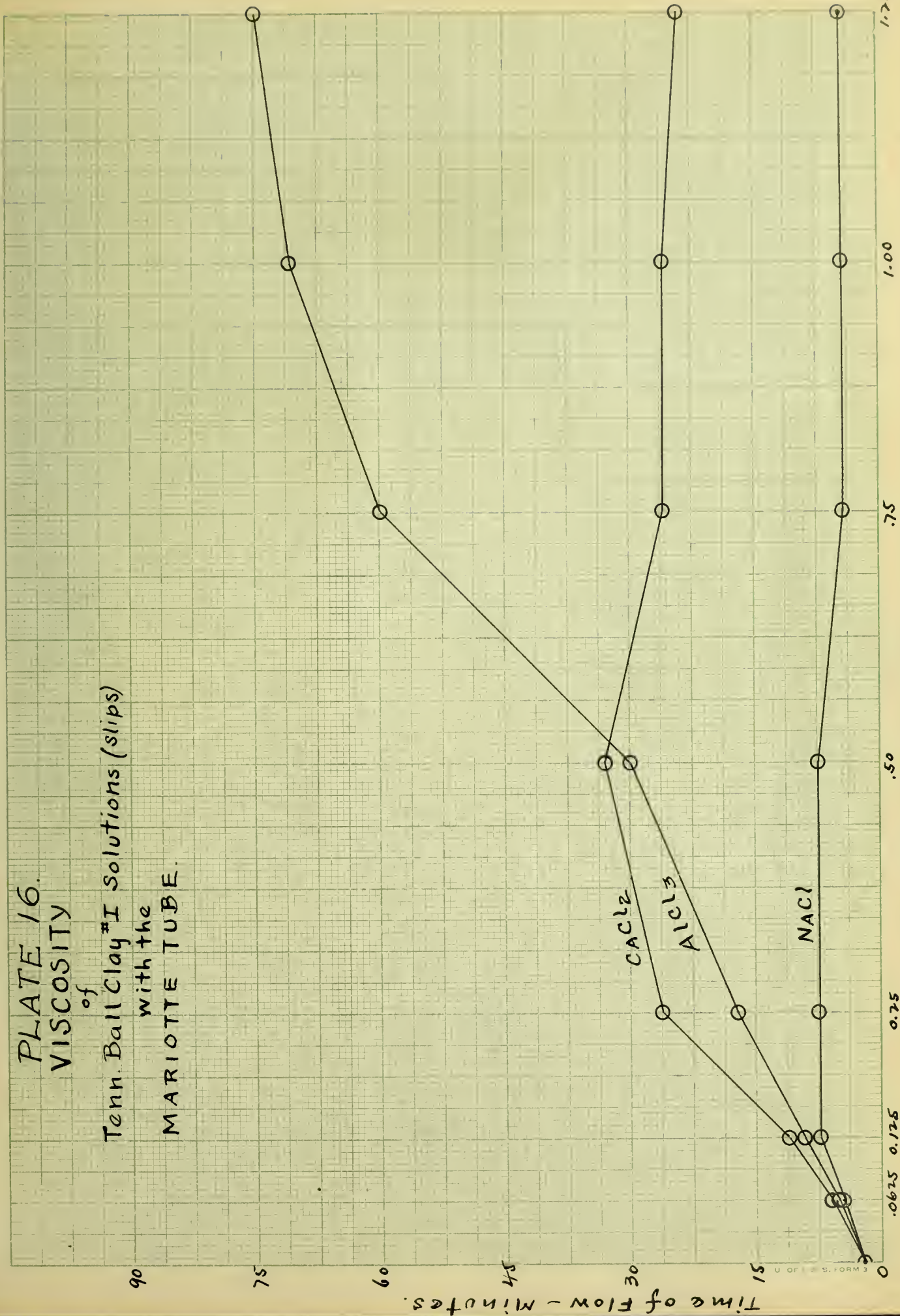
.75

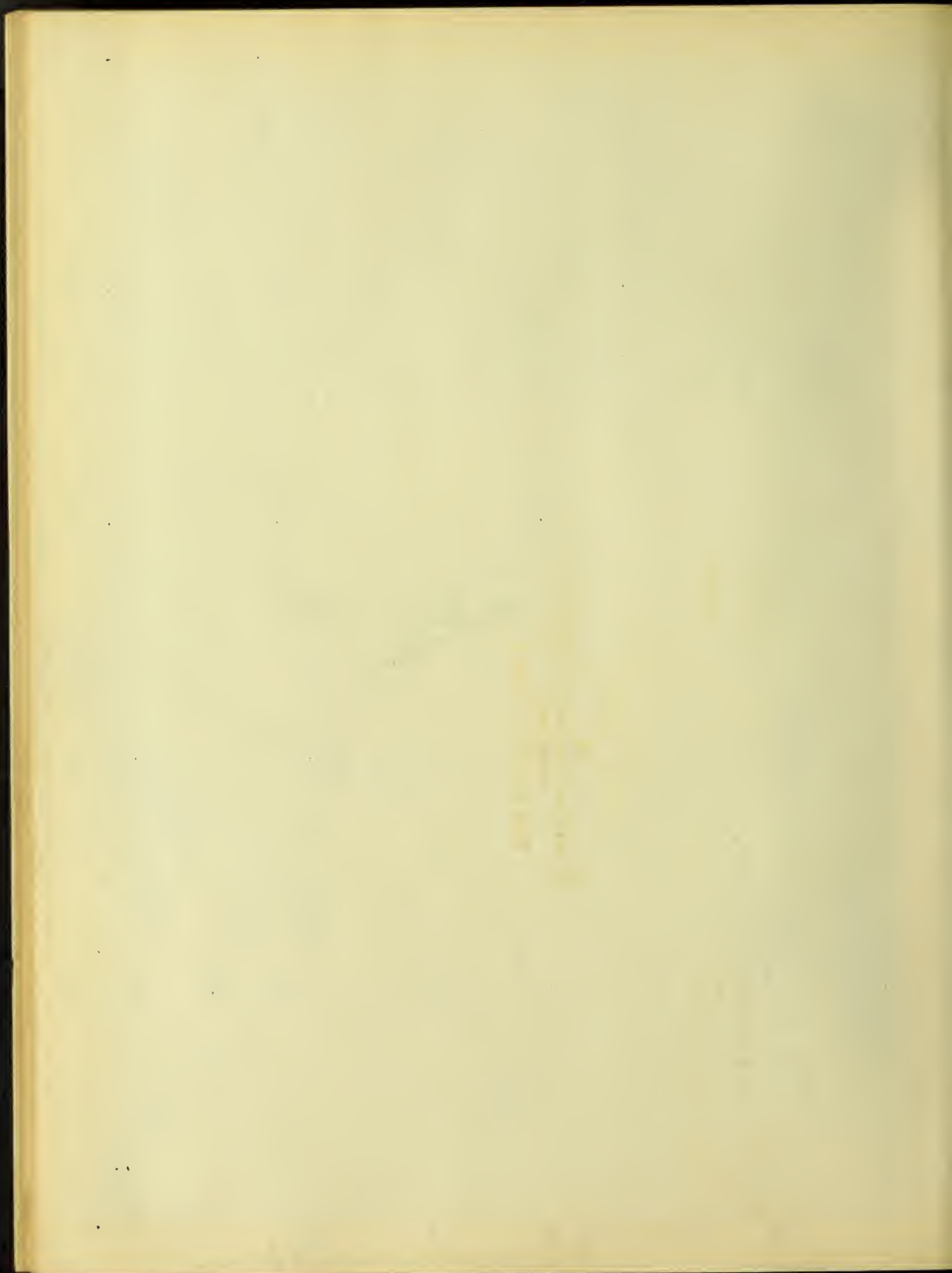
1.00

1.25

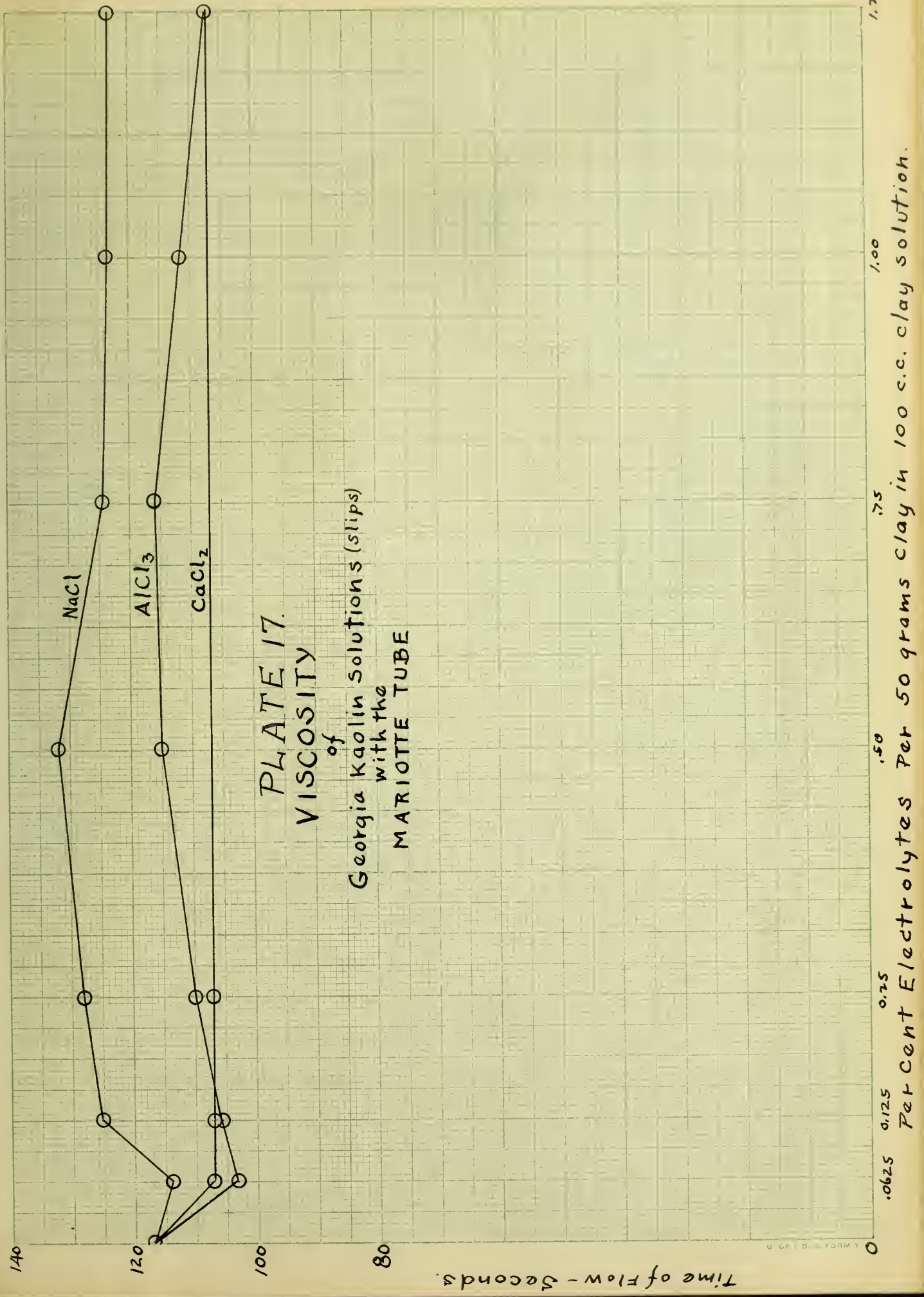
22-A

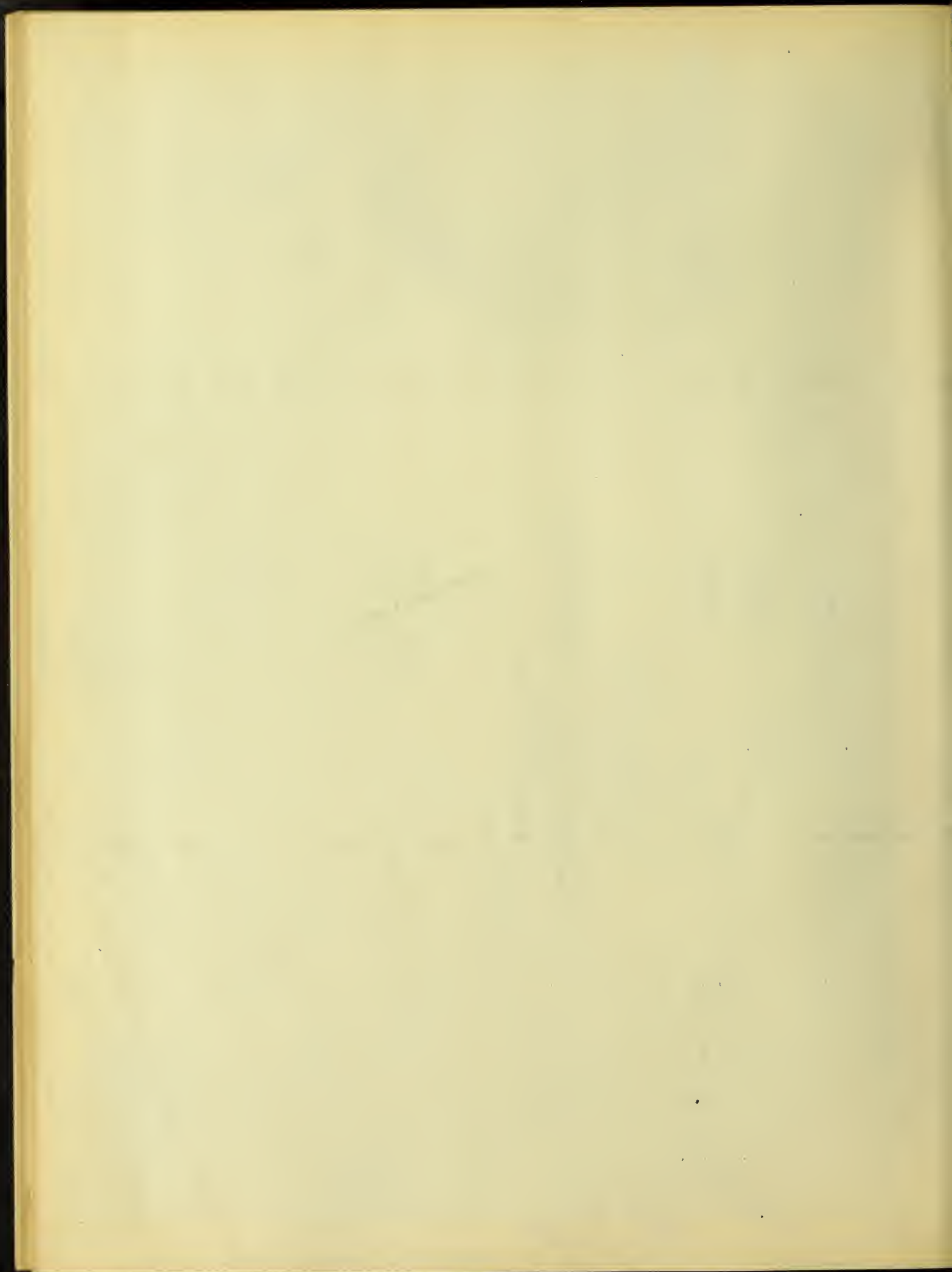
Percent Electrolytes Per 50 grams Clay in 100 c.c. Clay Solution.





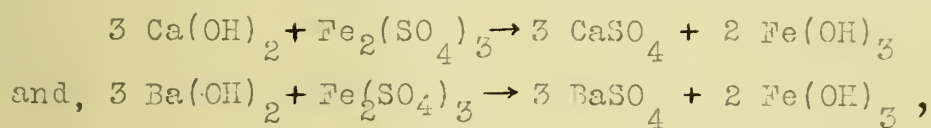






plotted in seconds along the ordinate axis in order to magnify the variations in viscosity. This work with neutral salts should be repeated several times in order to safely verify the effects of these salts on the viscosity of slips. As these tests were made only once and checked once for each concentration of salt, no further comment is necessary. It may be mentioned, that even neutral salts will have varying influences upon different clays which may be due to the kind as well as the quantity of colloid content in the clay.

Plate #18 shows the flocculating influence of  $\text{Ca}(\text{OH})_2$  and  $\text{Ba}(\text{OH})_2$  upon Tenn. Ball Clay #1, the former being the more active flocculating agent. Considerable iron is present in this ball clay, and possibly the following changes take place;



less soluble salts of calcium and barium being formed along with insoluble and gelatinous ferric hydroxide precipitate. This may account for the greater flocculating effect of  $\text{Ba}(\text{OH})_2$  with the ball clay slip than with the Georgia Kaolin slip. The  $\text{Ca}(\text{OH})_2$  was not soluble enough for using more than 0.30 per cent by weight of it in the slips tested. Higher per cents would undoubtedly have brought the curve sharply upward.  $\text{NaOH}$  and  $\text{KOH}$  are vigorous deflocculating agents. It will be noticed that  $\text{Ca}(\text{OH})_2$  which has a lower molecular weight is more effective as a flocculating agent than  $\text{Ba}(\text{OH})_2$  of greater molecular weight, while  $\text{KOH}$  of greater molecular weight than  $\text{NaOH}$  is a more effective deflocculating agent than the latter.

Plate #19 shows the effects of these same four electrolytes



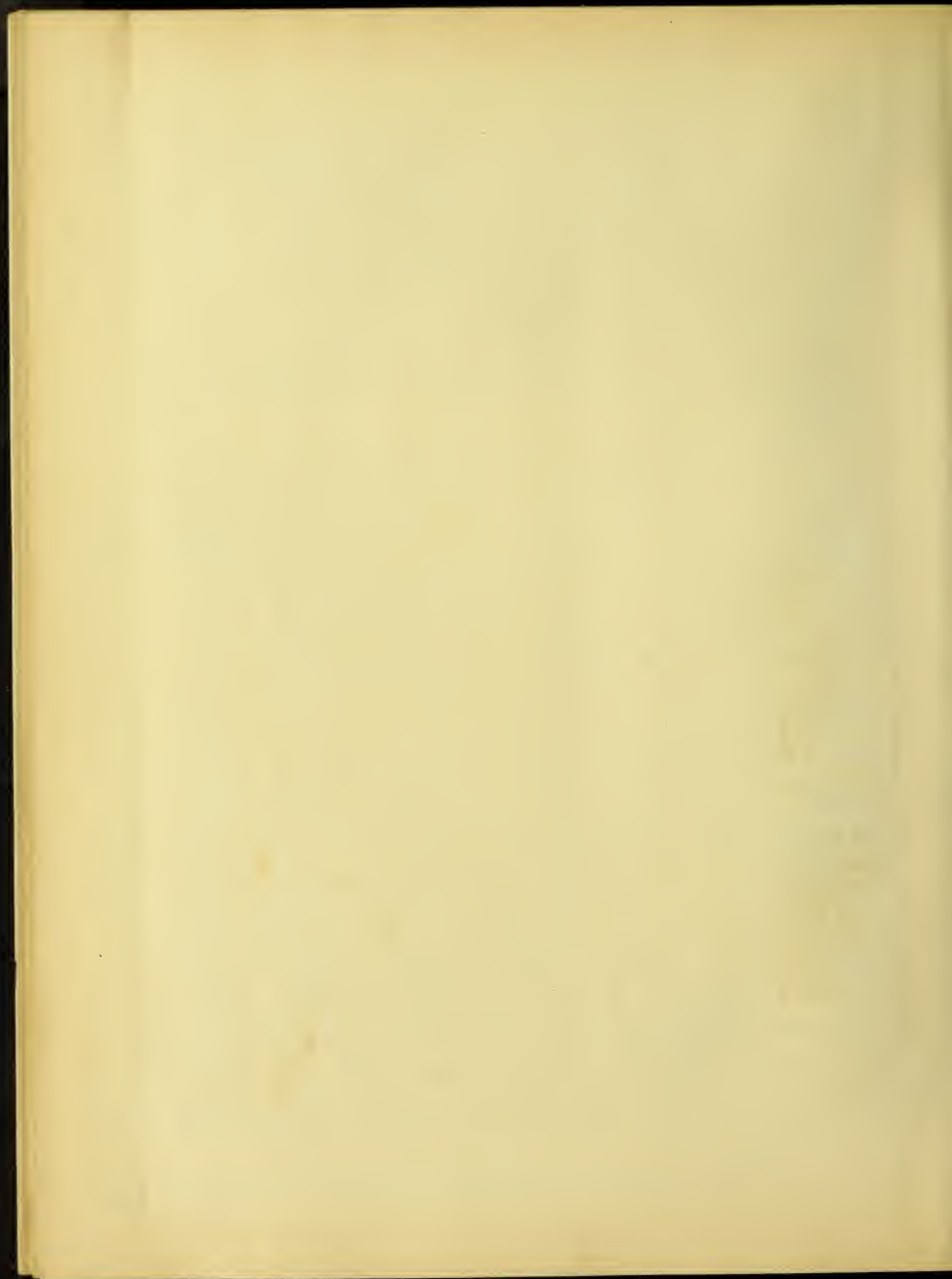
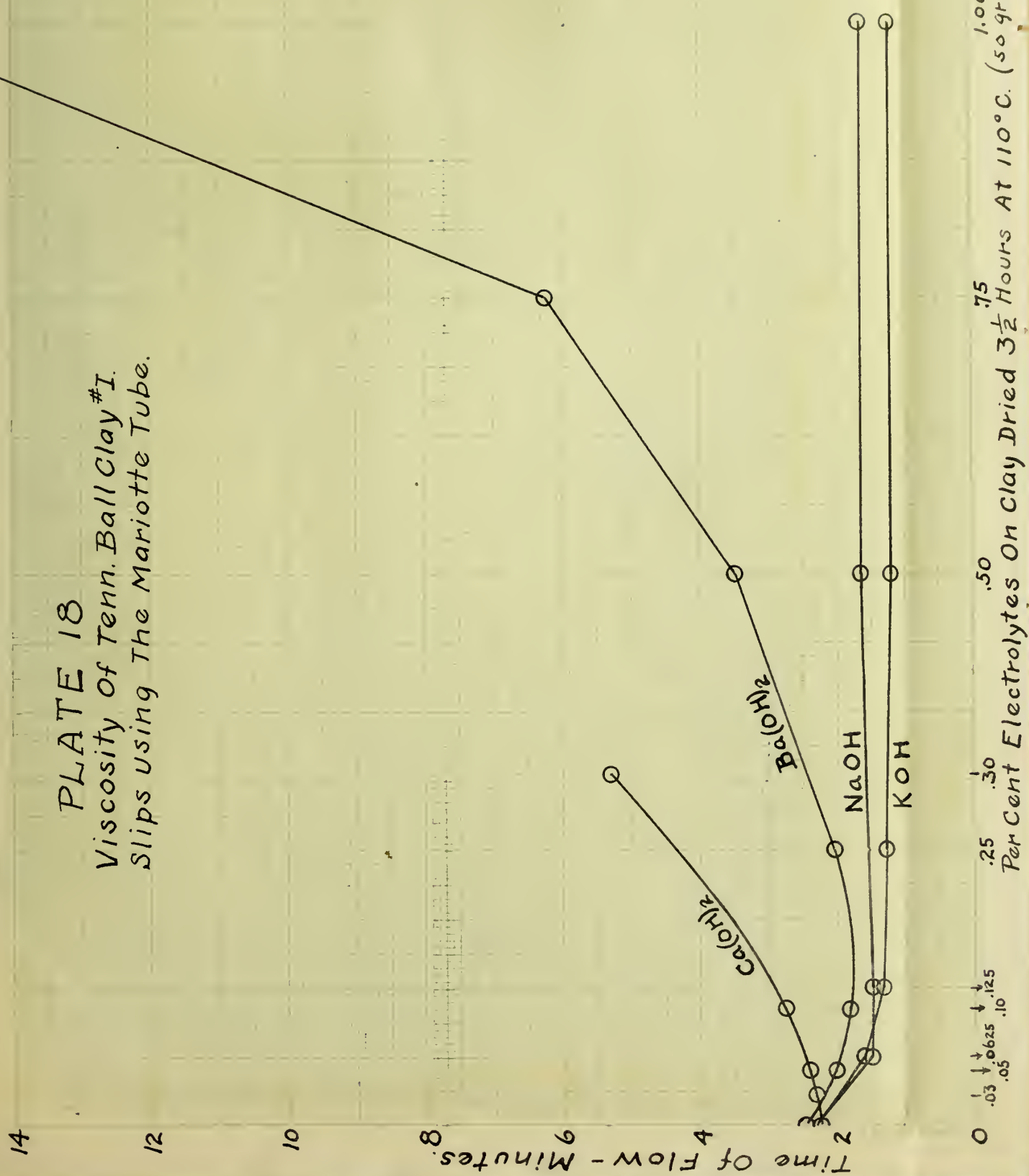


PLATE 18

Viscosity of Tenn. Ball Clay #1.  
Slips using The Mariotte Tube.



Per Cent Electrolytes On Clay Dried  $3\frac{1}{2}$  Hours At  $110^{\circ}\text{C}$ . (50 grams - 100 c.c.  $\text{H}_2\text{O}$ )

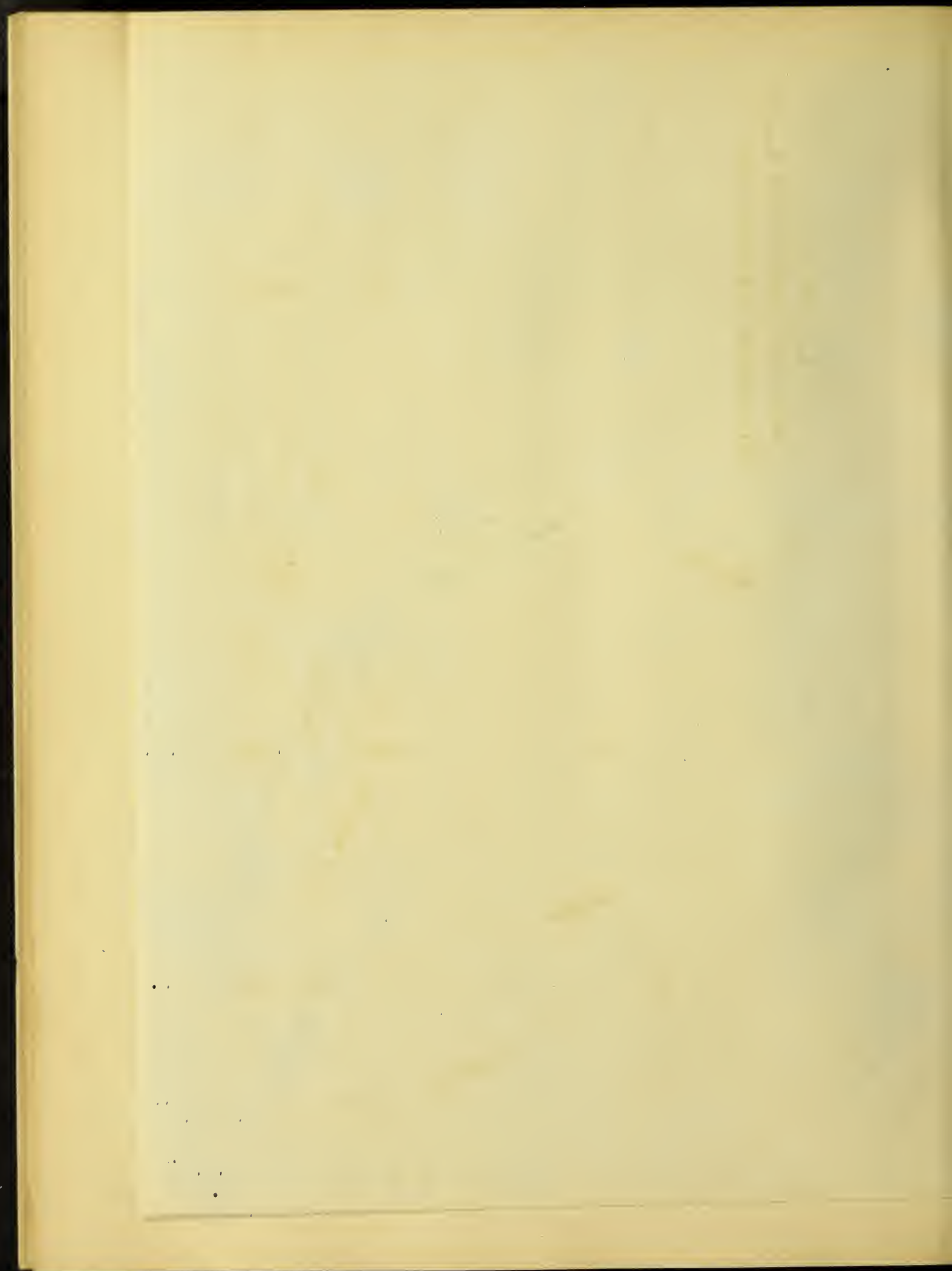
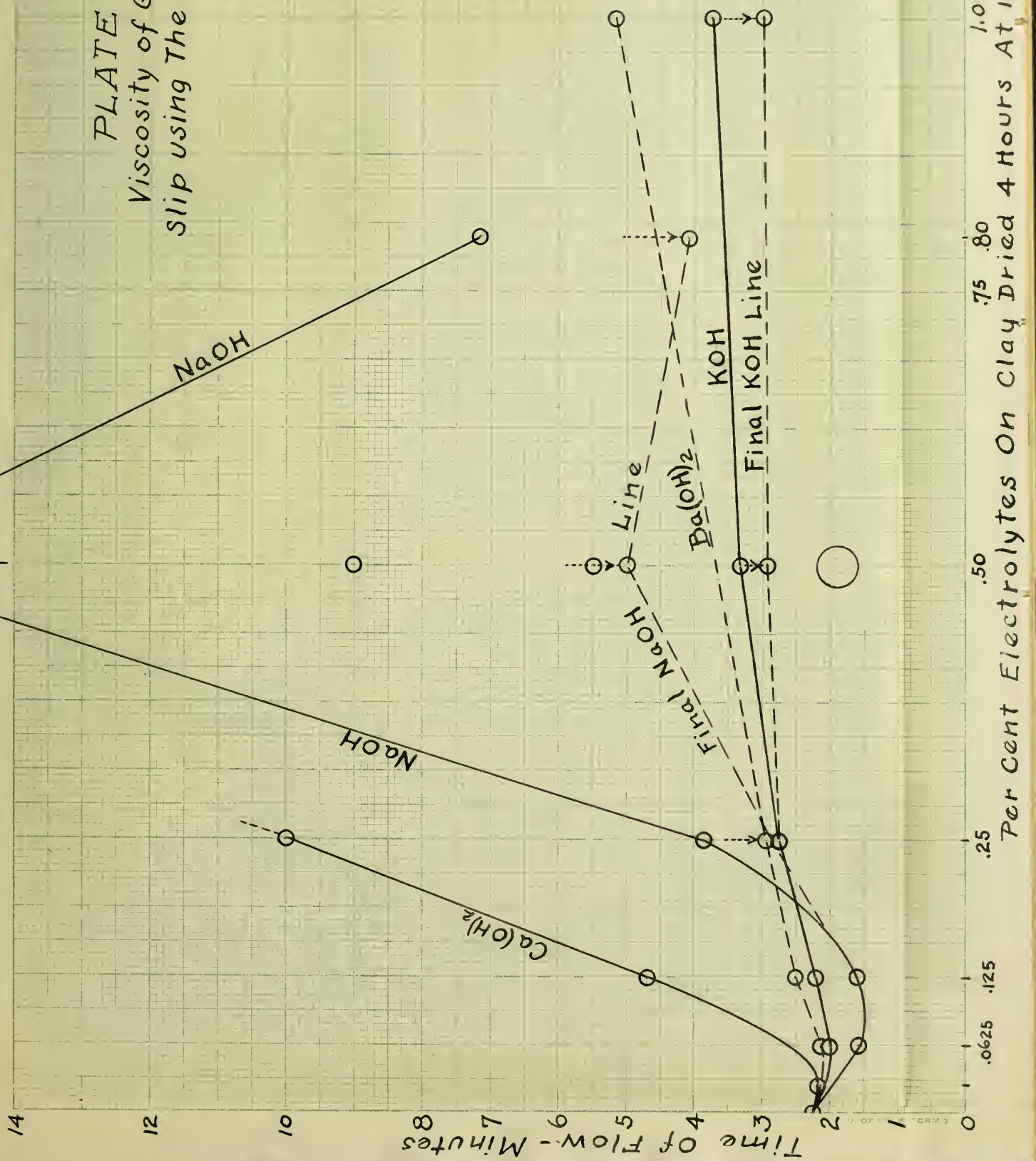
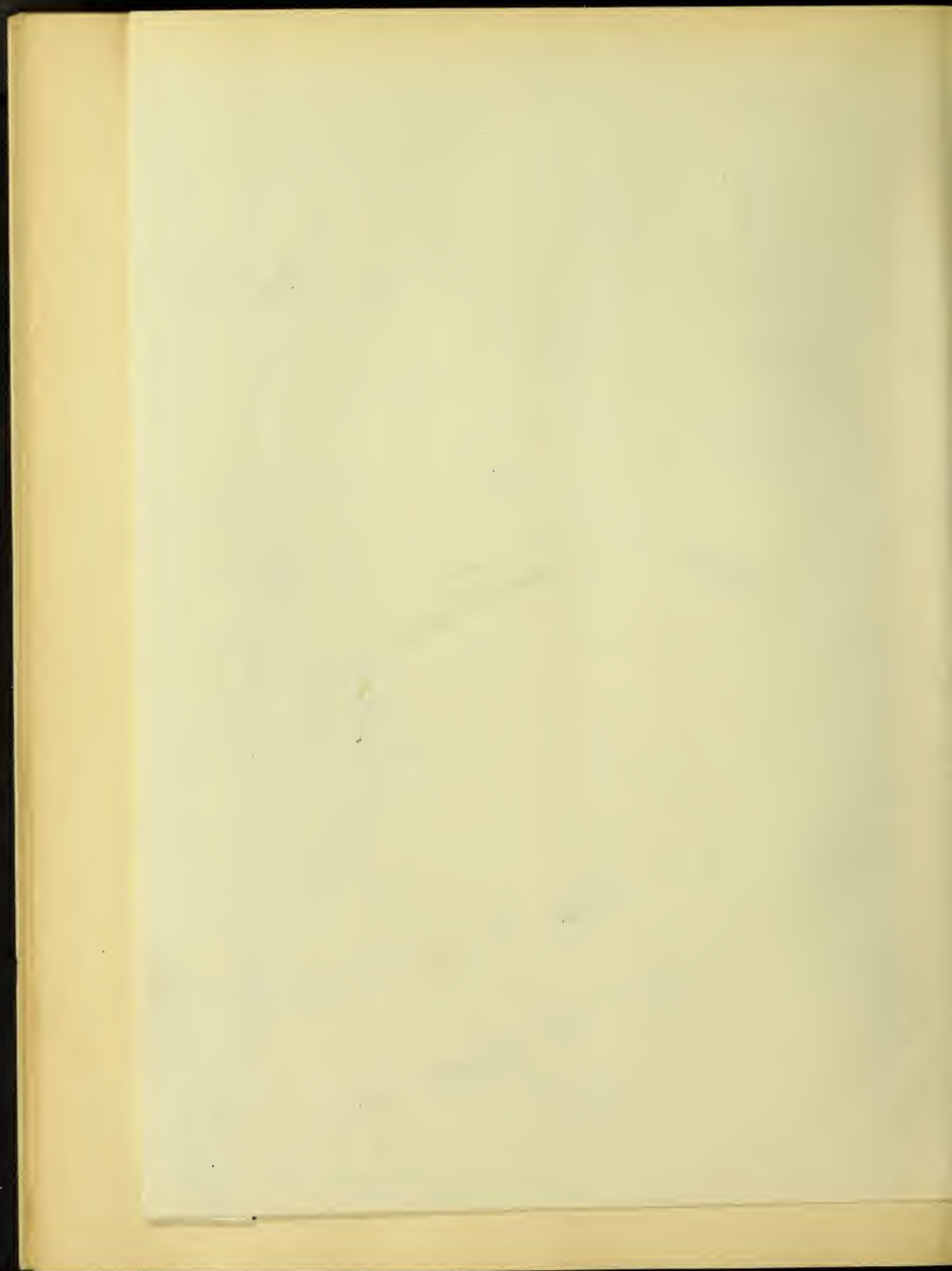




PLATE 19  
Viscosity of Georgia Kaolin  
Slip using The Mariotte Tube



Per Cent Electrolytes On Clay Dried 4 Hours At 110°C

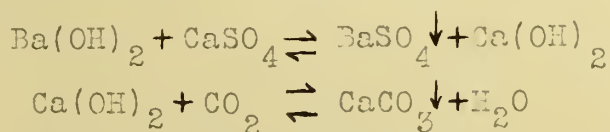




upon slips made with Georgia Kaolin.  $\text{Ca}(\text{OH})_2$  seems to show greater flocculating power and  $\text{Ba}(\text{OH})_2$  a little less so than these electrolytes show with slips made with Tenn. Ball Clay #1. Thus it is evident that  $\text{Ba}(\text{OH})_2$  will prevent efflorescence due to soluble sulphates and it will also tend to increase plasticity. The results obtained with  $\text{NaOH}$  and  $\text{KOH}$  were interesting. With concentrations greater than 0.125% of these hydroxides, the immediate effect upon the kaolin slip was that of flocculating agents. With 0.50%  $\text{NaOH}$ , the flocculating value was exceedingly high, but this effect speedily diminished on repeated viscosity tests with the same slip, as shown by the small circles, until a comparatively constant viscosity line could be plotted as shown by the broken line. When this slip with 0.50%  $\text{NaOH}$  was allowed to stand for 24 hours, open to the influence of the air and then the viscosity again determined, a value shown by the large circle was obtained, which indicated that after time had elapsed and the slip had been in contact with

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"It is possible that the  $\text{Ba}(\text{OH})_2$  acts somewhat as a deflocculating agent compared to  $\text{Ca}(\text{OH})_2$  according to the following reaction as given by Ashley<sup>1</sup>



The action may be on alkali sulphates,  $\text{Ba}(\text{OH})_2 + \text{Na}_2\text{SO}_4 \rightleftharpoons \text{BaSO}_4 \downarrow + 2\text{NaOH}$ , and hence deflocculation due to  $\text{NaOH}$ . Accordingly, the  $\text{Ba}(\text{OH})_2$  would not show its flocculating influence and stabilize the colloid gels until the soluble sulphates are disposed of as shown above in the form of insoluble  $\text{BaSO}_4$ . It is known that the Georgia Kaolin used contains considerable  $\text{CaO}$ , much of which is probably in the soluble form of  $\text{CaSO}_4$  and therein would lie the cause for the weaker flocculating effect of  $\text{Ba}(\text{OH})_2$  on Georgia kaolin slip than on Tenn. Ball clay #1 slip, for the concentrations used."

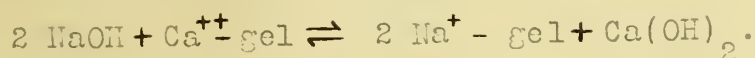
1. Trans. Am. Cer. Soc. Vol. 12.



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air, the NaOH proved itself a deflocculating agent as was the case with slips of Tenn. Ball Clay #1. When contact with air is not allowed, the viscosity values for the different concentrations of NaOH and KOH are not appreciably decreased but remain close to the values as shown by the full line curves. The viscosity values for  $\text{Ca}(\text{OH})_2$  and  $\text{Ba}(\text{OH})_2$  were fairly constant for one hour after first testing but no tests were made after allowing these slips to stand for longer periods. Böttcher<sup>1</sup> while doing similar work experienced what he called super-stiffening of his slips and Ashley<sup>2</sup> offered "delayed chemical action" as an explanation. The following is offered as an analysis of this action.

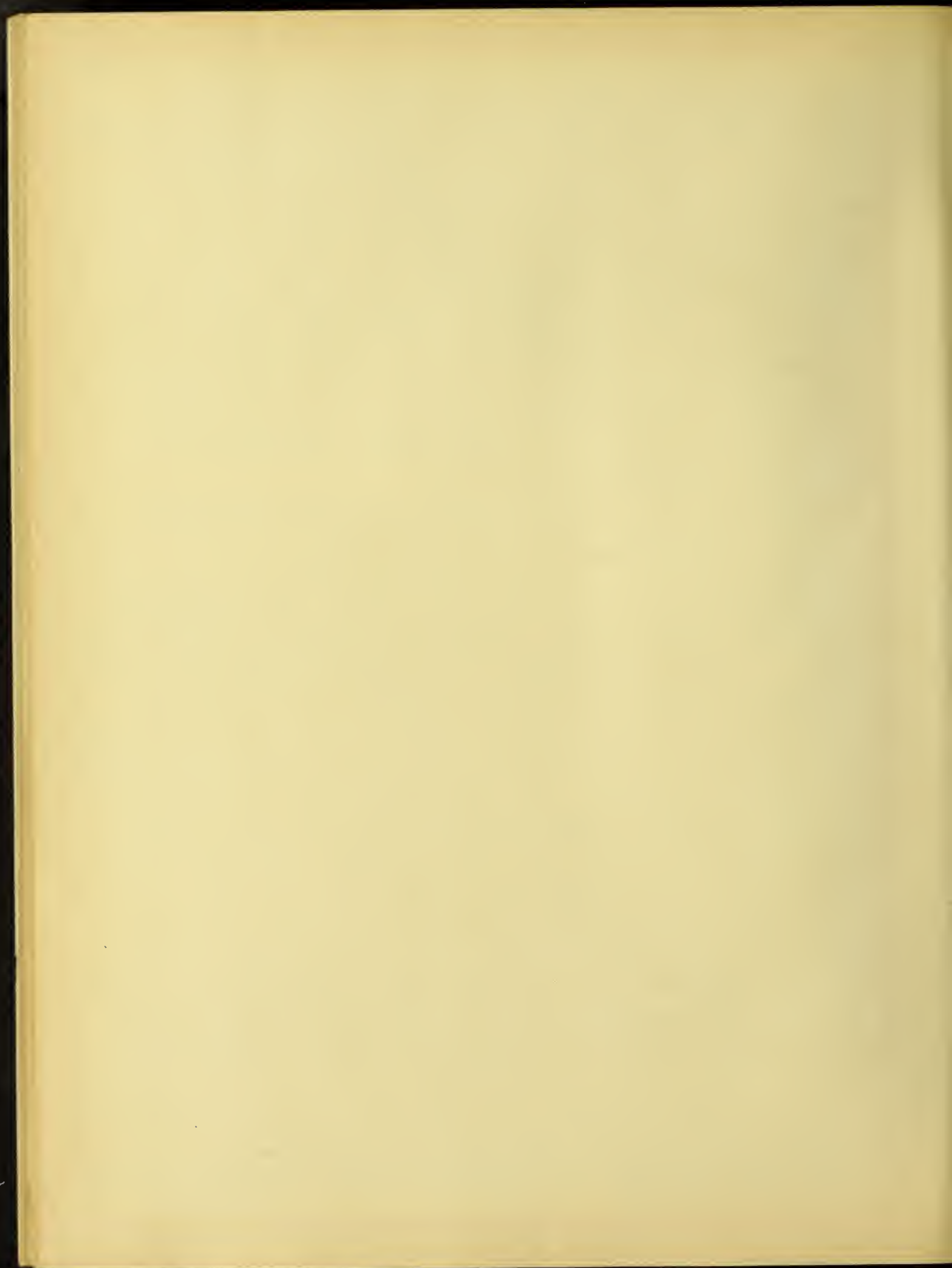
The lime of the kaolin is probably acted upon as follows:



If contact with air is not allowed, the colloids remain coagulated giving high viscosity values. Otherwise the following reaction takes place:  $\text{Ca}(\text{OH})_2 + \text{CO}_2 \rightleftharpoons \text{CaCO}_3 \downarrow + \text{H}_2\text{O}$ , in which case the stabilizing influence of the lime is reduced to a minimum, allowing the soda gels to change to the sol state and thereby deflocculate the colloids and reduce the viscosity. With excess NaOH we have the deflocculating effect occurring immediately upon testing the slip as shown by the NaOH curve on plate #19. This phenomena with Georgia kaolin is not shown in such a marked form when KOH is used. Similar reactions take place but the action is not so much delayed as with NaOH, due possibly, to the increased speed of migration which the  $\text{K}^+$  ions have over the  $\text{Na}^+$  ions, caused by the greater molecular weight of the  $\text{K}^+$  ion. It would be interesting to observe whether lithium

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1. Sprech. Vol. 32, Part I, 1909, Nos. 10, pages 134-135.

2. "The Technical control of colloids in clays. "Trans. Am. Cer. Soc. vol. 12, page 790.



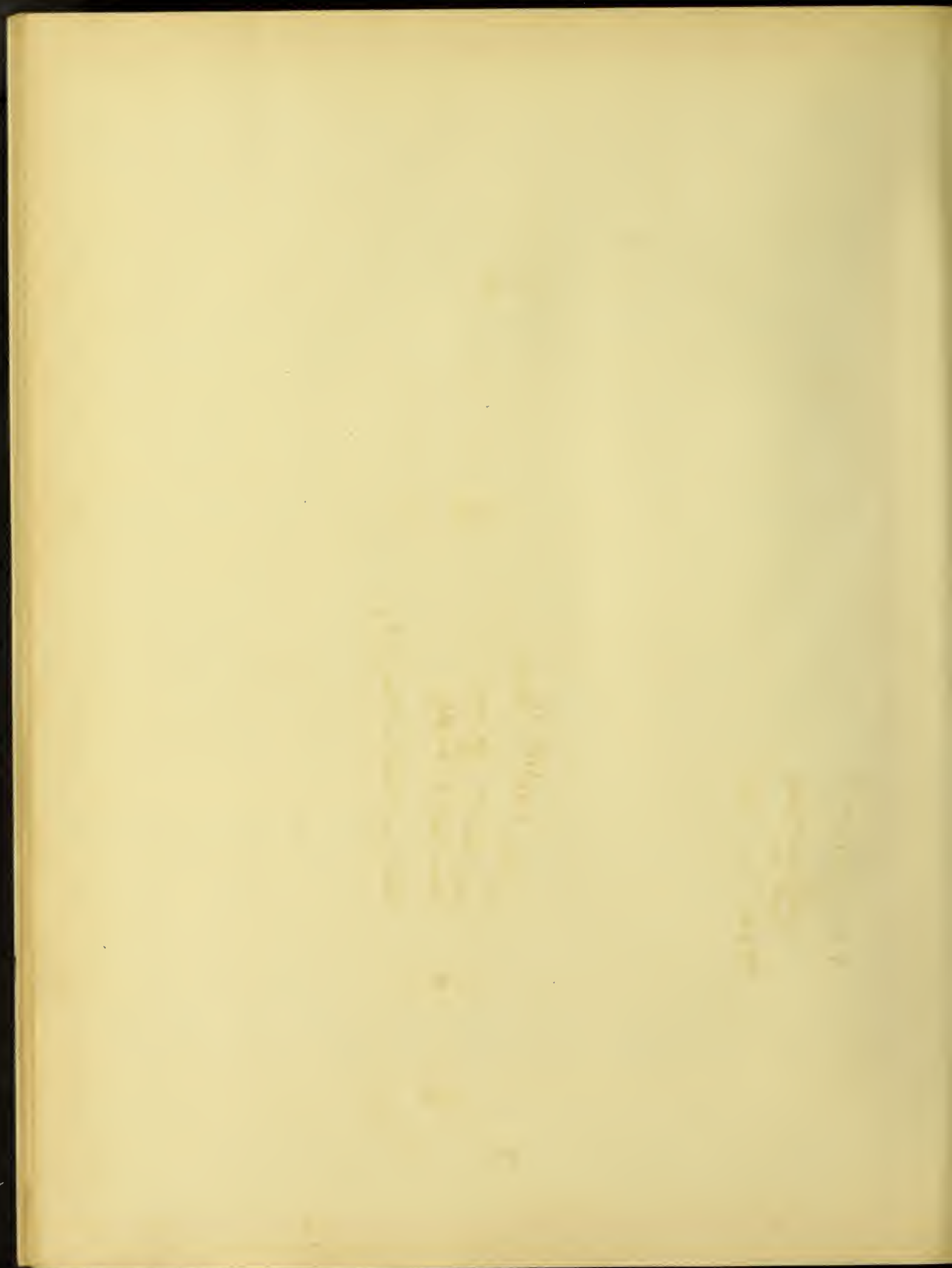


hydroxide would not have caused a still greater delay in this action for the  $\text{Li}^+$ -ion, having a molecular weight of only "7", has a speed of migration which is less than that of the  $\text{Na}^+$ -ion. Böttcher's<sup>1</sup> work gives some foundation for this reasoning, for it took a smaller molecular equivalent of  $\text{LiOH}$  than either  $\text{NaOH}$  or  $\text{KOH}$  to produce this immediate increase in viscosity or "super-stiffening" as he calls it, and after 24 hours standing the viscosity or stiffness was not as thoroughly reduced for  $\text{LiOH}$  slips of the higher concentrations as it was with both the  $\text{NaOH}$  and  $\text{KOH}$  slips. Böttcher's results do not show such a marked difference between the use of  $\text{NaOH}$  and  $\text{KOH}$  as shown in this work but his slips were much thicker which may account for the difference. 50g per 64 c.c. It seems very evident that the speeds of migration of the ions play an important part in colloid reactions for clay solutions when electrolytes are added. Plate #20 shows the liquifying or deflocculating influence of  $\text{Na}_2\text{CO}_3$  and  $\text{Na}_2\text{SiO}_3$  upon slips of Georgia kaolin and Tenn. Ball Clay #1. Only 0.125 per cents of these reagents are necessary to give minimum viscosity.

Using the same kind of mariotte tube for measuring viscosities of clay slip, Green<sup>2</sup> and Baugh found that it took about 0.6% of  $\text{Na}_2\text{CO}_3$  and  $\text{Na}_2\text{SiO}_3$  to obtain a minimum value of viscosity. This they obtained by using 68 gr. clay to 110 c.c. water, and allowing 200 c.c. of slip to flow from the tube. It was found that the velocity of outflow was appreciably changed as the slip lowered in the tube. In this work the writer's tests were made with smaller

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1. Sprech. Vol. 42, part I, 1909, No.10, pp. 133,134,135.

2. "Studies on Clay Slip," Trans. Eng. Cer.Soc. 1905-07 pp. 165-66





# PLATE 20. VISCOSITY

of  
CLAY SOLUTIONS  
with the

MARIOTTE TUBE

180

Time of flow - Seconds.

120 60

Georgia Kaolin -  $\text{Na}_2\text{CO}_3$

Tenn. Ball #1 -  $\text{Na}_2\text{SiO}_3$

Tenn. Ball #1 -  $\text{Na}_2\text{CO}_3$

Georgia Kaolin -  $\text{Na}_2\text{SiO}_3$

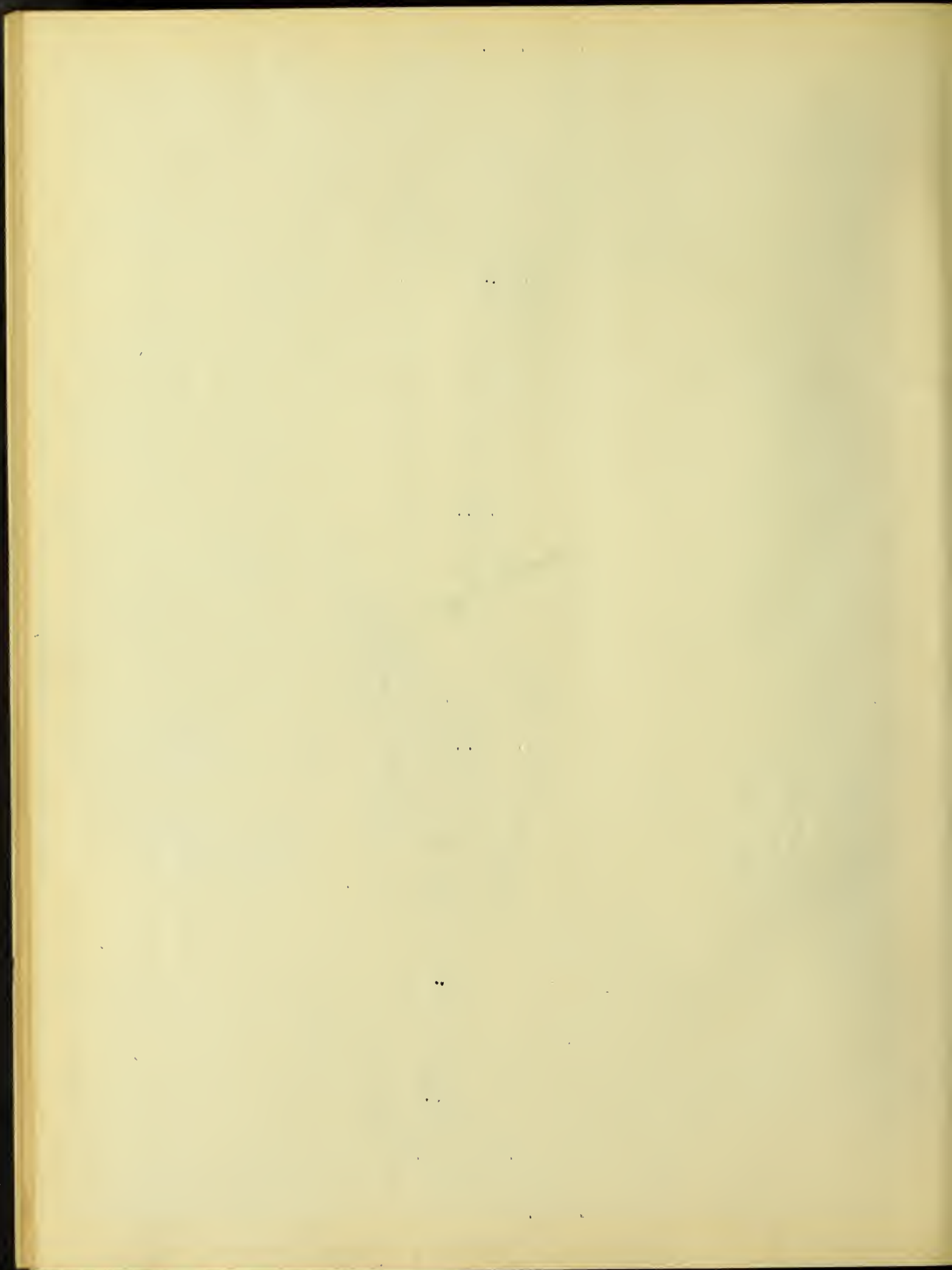
.0625 .125 .25 .50 .75 1.00 1.25

Per Cent Electrolytes Per 50 grams clay in 100 c.c. clay solution.

26-A

U. OF. S. S. FORM 3

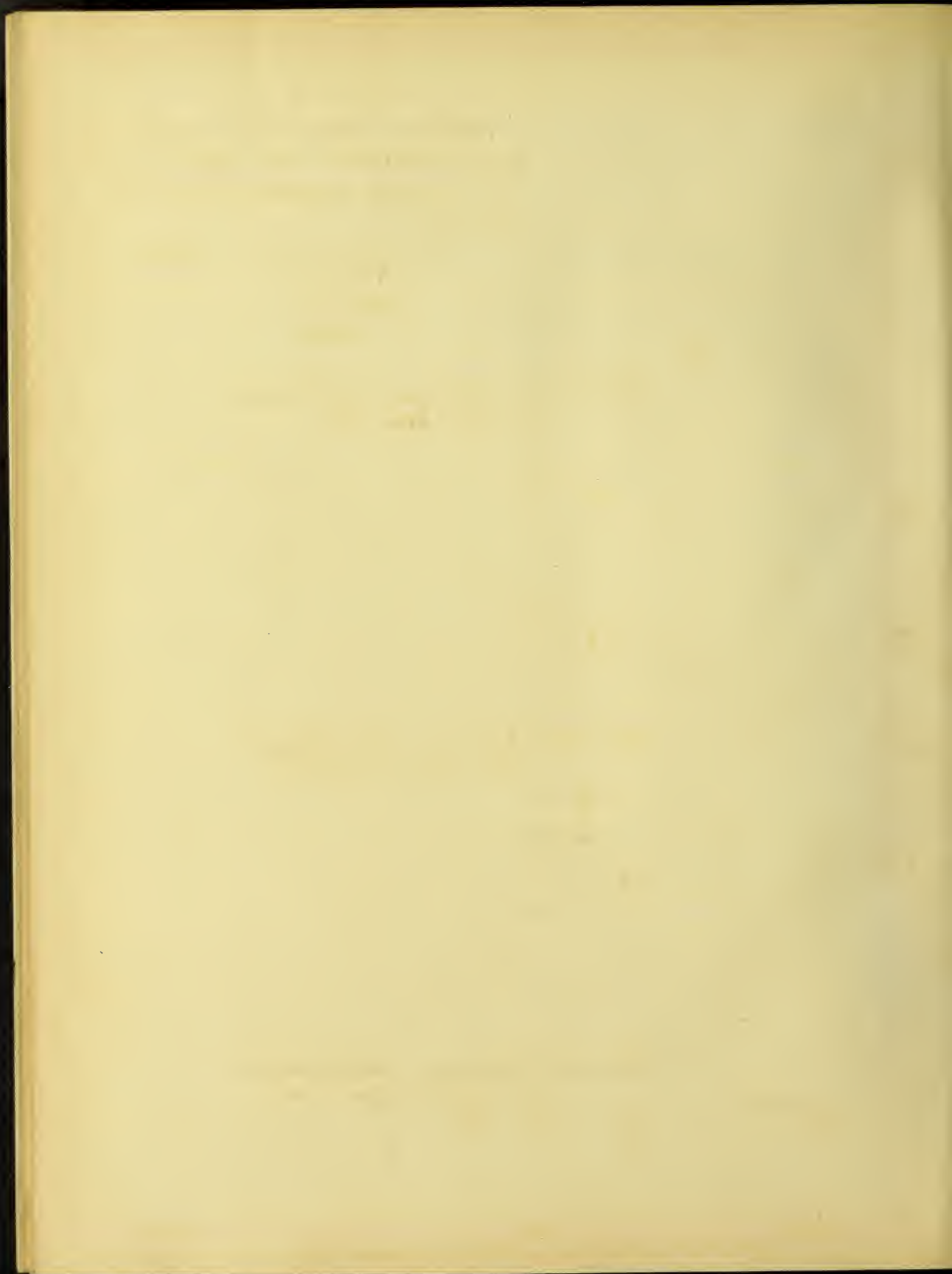




volumes of slip, observing the time required for the slip to sink in the tube from one level to the next. Between these levels the velocity of efflux is practically constant.

#### VIII. Volume Shrinkages of Casting Slips Using Electrolytes.

In order to determine the effects which  $\text{Na}_2\text{CO}_3$ ,  $\text{Na}_2\text{SiO}_3$ , and  $\text{NaOH}$  have upon the volume shrinkages of casting slips, the work represented by plates #21 and #22 was accomplished. The shrinkages are calculated to three bases and consequently three sets of curves are shown on both plates. The shrinkage is greatly affected by 0.125% electrolytes,  $\text{Na}_2\text{SiO}_3$  having the greatest influence. With  $\text{Na}_2\text{SiO}_3$  and Georgia kaolin, this electrolyte could not be used in amount greater than 0.50% for the cast body became so weak in structure that it could not be removed from the mold in one piece and its volume determined when dry. The sample of slip with 0.50%  $\text{NaOH}$  was allowed to stand 24 hours excluded from the air before testing and making it up to the constant viscosity used in this work for casting. Again this same stiffening of Georgia kaolin slip occurred and considerable water had to be added in order to get a constant viscosity before casting. This is the cause for the lack of similarity in the  $\text{NaOH}$  curves for the two clays. If the  $\text{CO}_2$  in the air had been allowed to affect the kaolin slip on standing for 24 hours, the shrinkage for the kaolin slip with 0.50%  $\text{NaOH}$  would have been greatly reduced from its value as shown on plate #21 and would have approximated a value that would make the curve similar to the others on this plate as well as those of plate #22. In this work, the clays were dried to constant viscosity and then slips with electrolyte solutions were made up to constant





## PLATE 21.

Volume shrinkages produced  
by electrolytes used with clay as  
casting slip, keeping viscosity  
constant.

Georgia Kaolin Slips.

1.  $\text{Na}_2\text{SiO}_3$

2.  $\text{Na}_2\text{CO}_3$

3.  $\text{NaOH}$ .

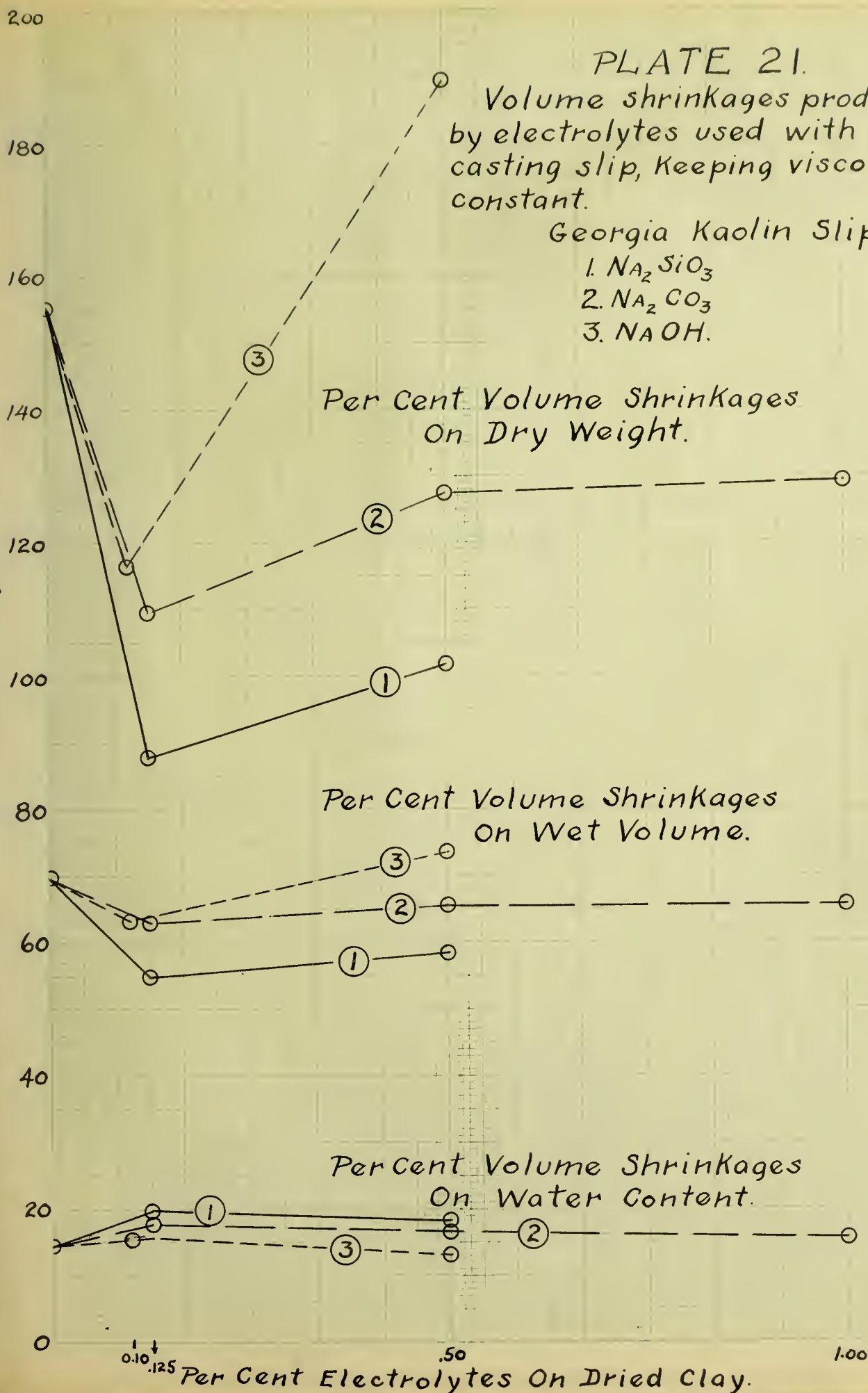
Per Cent Volume Shrinkages

Per Cent Volume Shrinkages  
On Dry Weight.

Per Cent Volume Shrinkages  
On Wet Volume.

Per Cent Volume Shrinkages  
On Water Content.

Per Cent Electrolytes On Dried Clay.





Volume Shrinkages Produced By Electrolytes  
Used With Clay As Casting Slip Keeping Viscosity  
Constant.

# PLATE 22.

Tennessee Ball clay #I.

1.  $\text{Na}_2\text{SiO}_3$

2.  $\text{Na}_2\text{CO}_3$

3.  $\text{NaOH}$

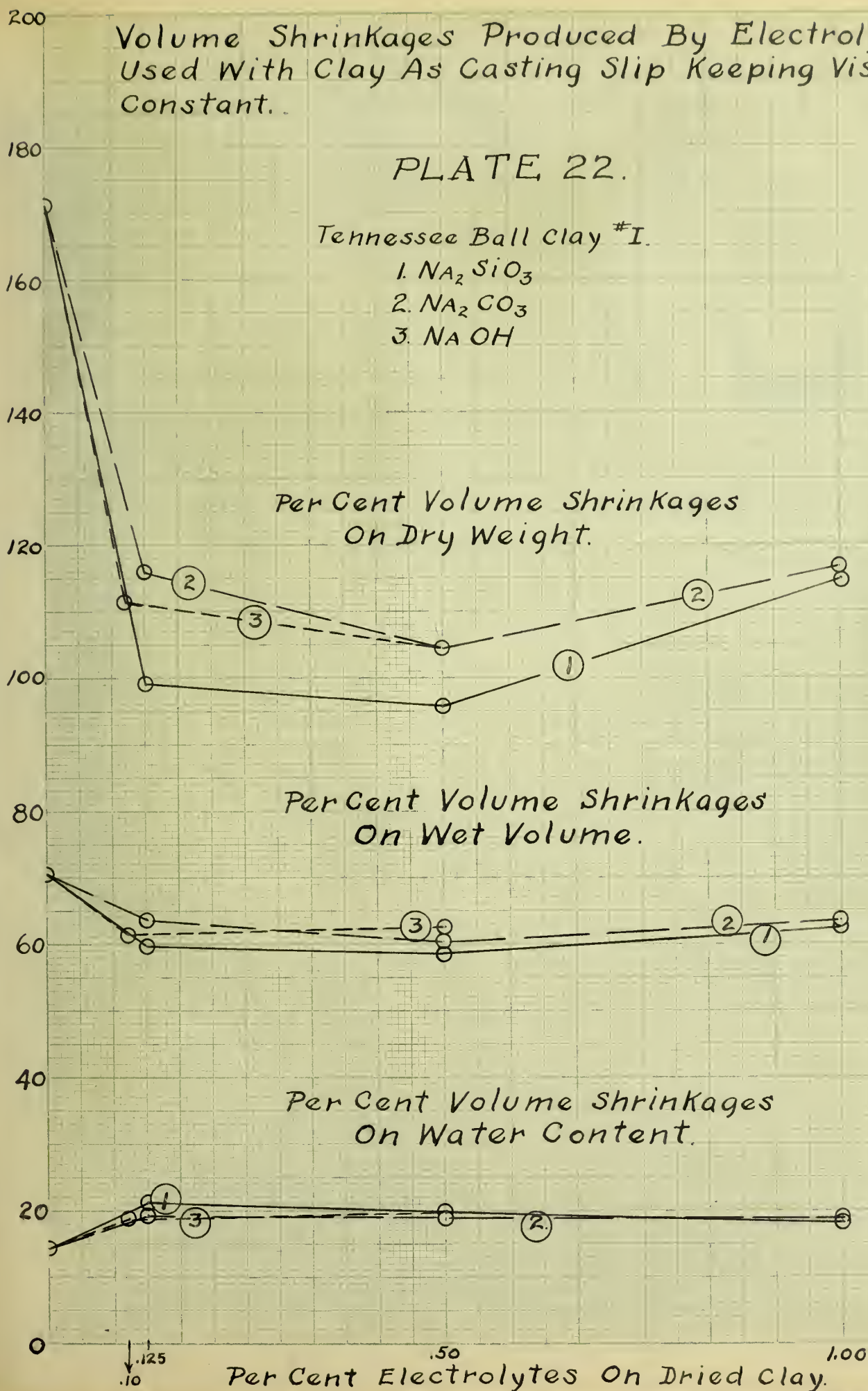
Per Cent Volume Shrinkages

Per Cent Volume Shrinkages  
On Dry Weight.

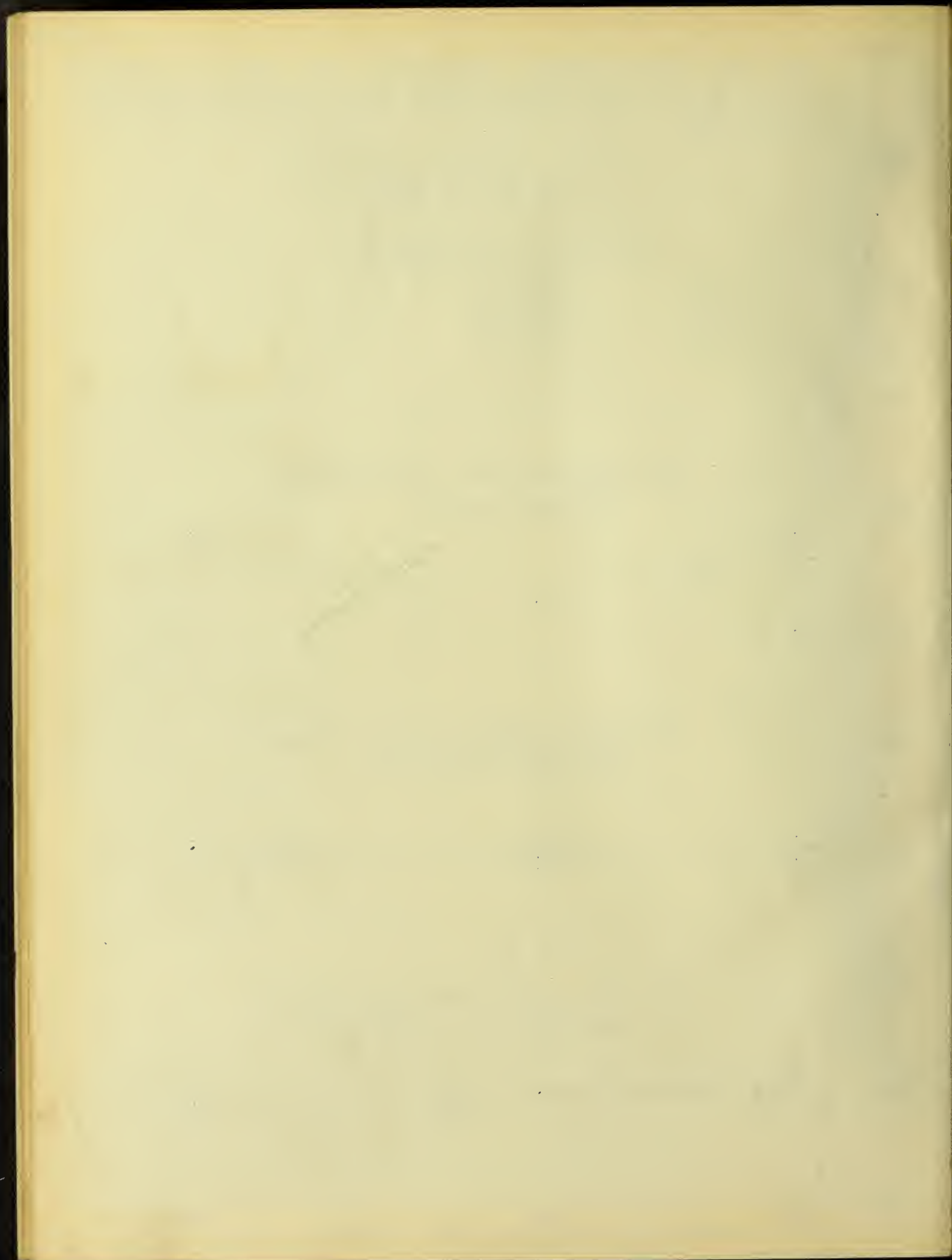
Per Cent Volume Shrinkages  
On Wet Volume.

Per Cent Volume Shrinkages  
On Water Content.

Per Cent Electrolytes On Dried Clay.







viscosity by varying the amounts of water needed. These slips were poured from a burette before settling could take place into plaster of paris molds care being taken to use the same volume of slip to fill the molds. The shape of the cast piece when dried was that of figure 2. The volumes were determined in the usual way after first soaking the dried pieces in petroleum over night. The larger quantities of electrolytes used caused such thorough deflocculation of the slips that the dried cast pieces when broken open showed how completely the fine colloidal material had been separated from the larger grains of clay, allowing these grains to settle to the bottom of the cast piece while the fine colloidal clay settled on top. Such thorough deflocculation would tend to weaken the piece by causing a structure which is not homogeneous. The cast pieces of Tenn. Ball clay for 0.50% of NaOH, and 0.50% and 1.0% of  $\text{Na}_2\text{SiO}_3$  showed hardened, dull black surfaces when dried due to accumulation of colloidal carbon drawn to the surfaces during evaporation.

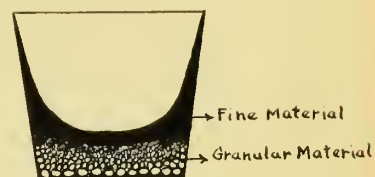


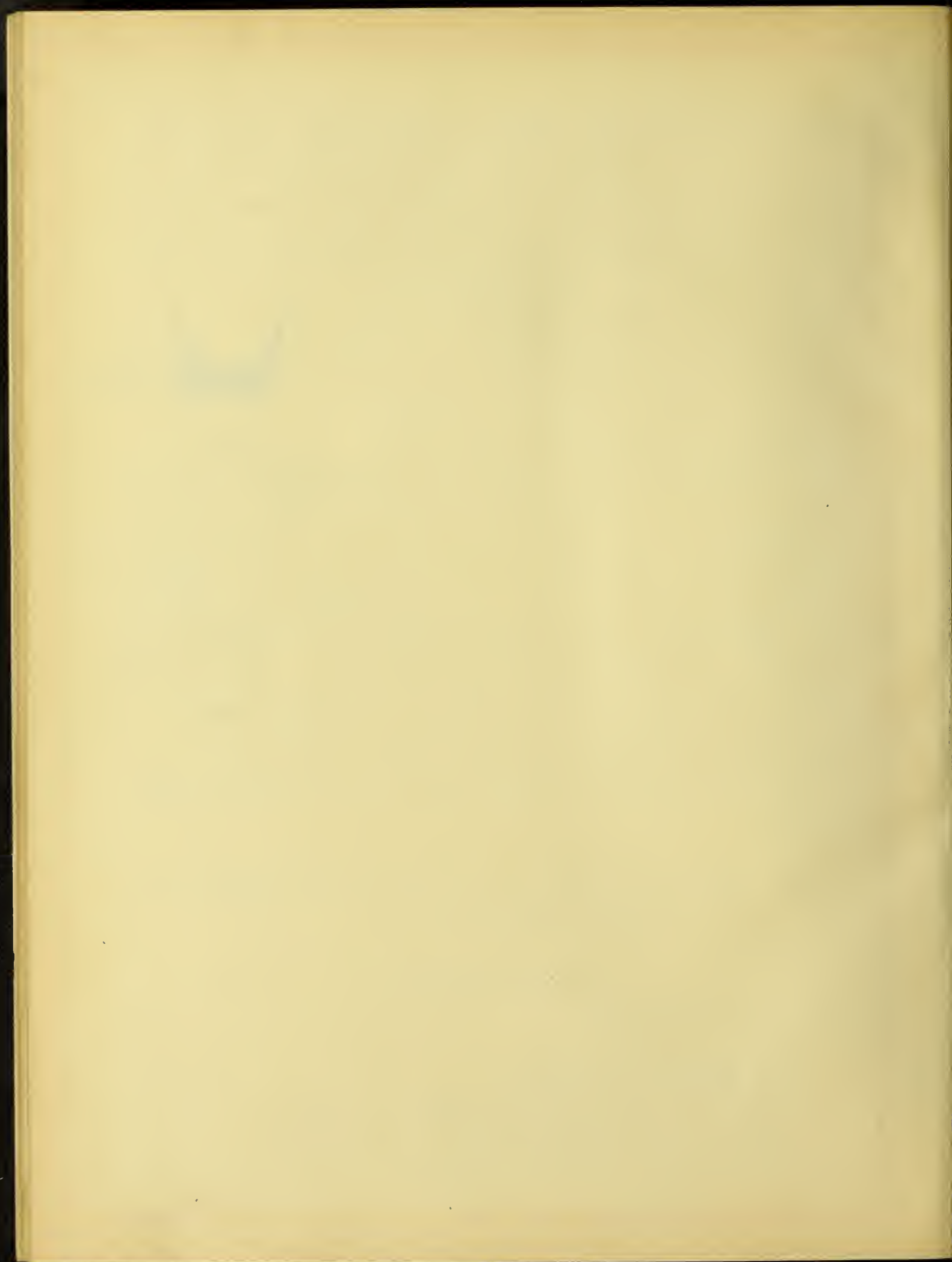
Fig.2.

## IX. The Bearing of Colloids in Clay Upon the Metallurgical and Ceramic Industries.

### Ceramic Industries.

#### I. In casting Processes.

- (A) Pottery (whiteware)
- (B) Glass pot manufactory
- (C) Zinc muffles and Gas Retorts
- (D) Large crucibles for the steel industries.
- (E) Glass furnace materials
- (F) Glass and Gas furnace blocks.





## II. Improvement of Clays,

(A) By removing bases combined with colloid gels,

1. Removing iron improves color.
2. Substituting  $H_2$  or Al for colloidal Ca, Mg, Fe, Na, and K makes fire clay less fusible.
3. Cut down shrinkage of some refractory lining materials like bauxite for example.
4. Wash out refractory bases in pottery clays with alkaline salt solutions to lower maturing temperature of pottery ware.
5. Colloidal carbon can be removed from clay if necessary by use of deflocculants as  $Na_2SiO_3$  or  $Na_2CO_3$ .

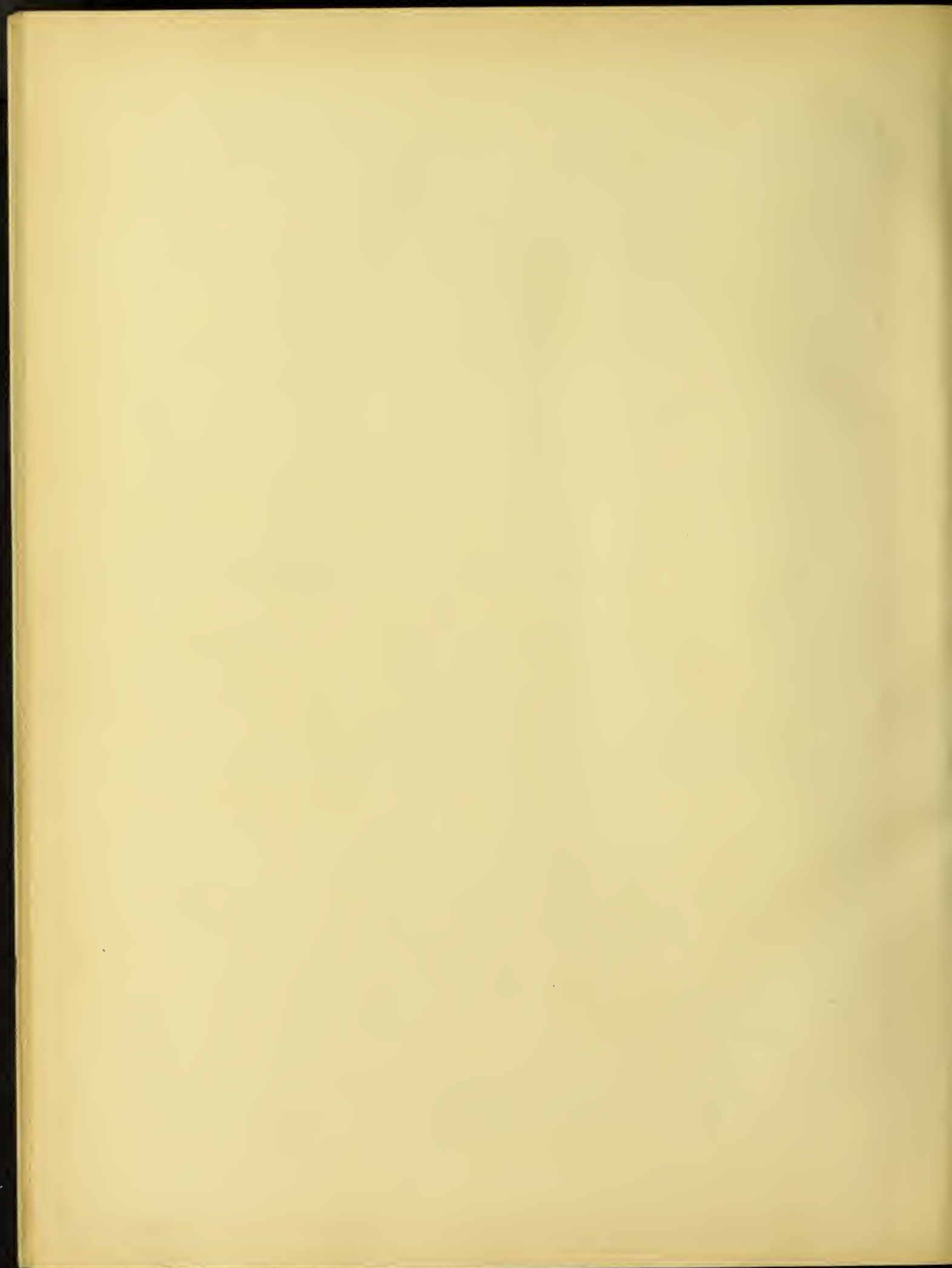
(B) By increasing plasticity.

1. By storing and ageing the clay.
2. With addition of organic colloids
3. With  $BaCO_3$  or  $Ba(OH)_2$  to prevent efflorescence of soluble salts.

III. Attempts to remove colloid matter from clays and thereby use granular or colloidal clay as we wish it in the industries. Use the concentrated colloid matter in place of Fuller's earth for uses which the latter earth has at present.

IV. Attempting to obtain a satisfactory method for measuring the plasticity of clays.

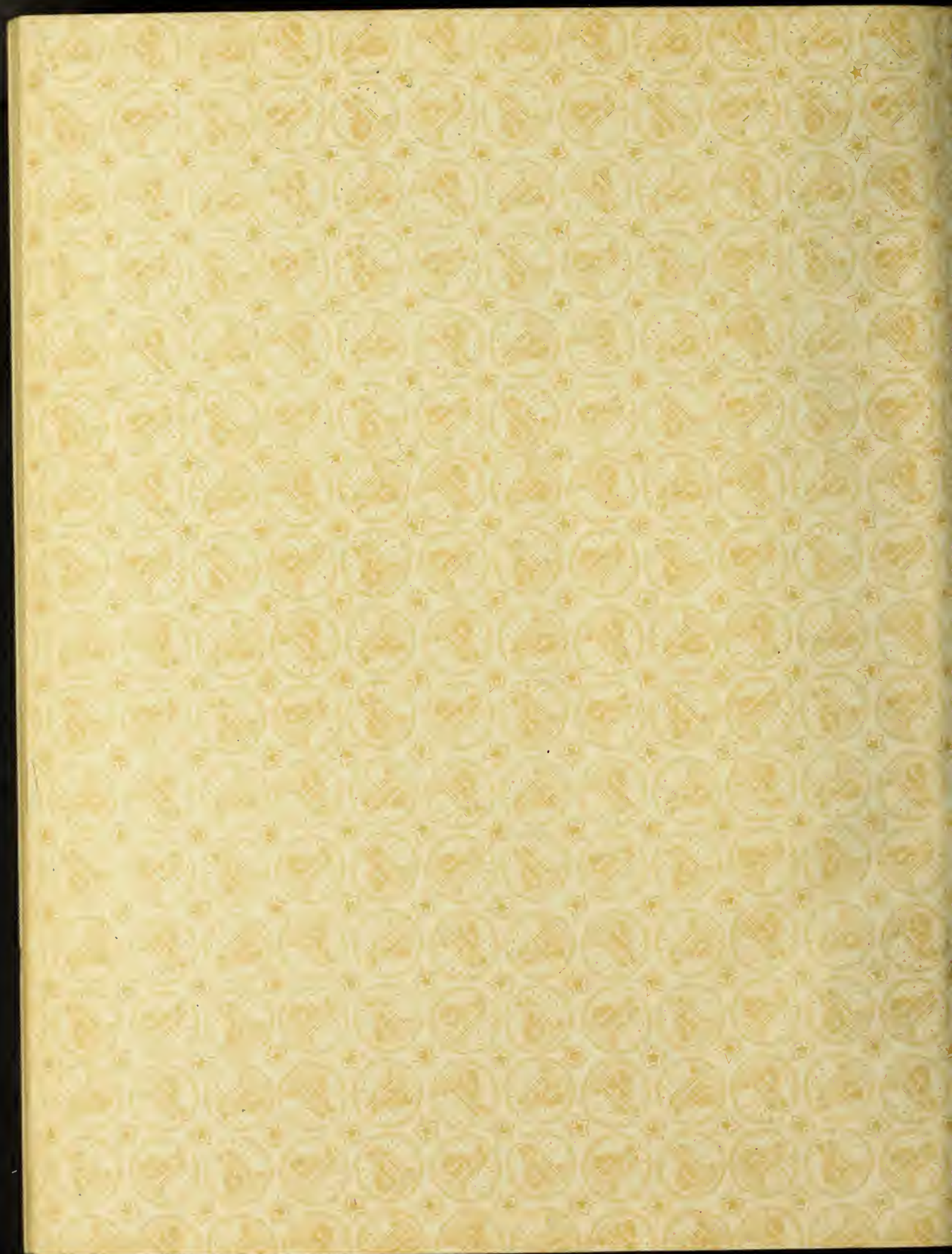
V. A better knowledge of clay colloids should assist us in problems of fitting slips and enamels to clay bodies.



## Metallurgical Industries.

- I. To the geologist the phenomenon of the sedimentation of mud and slimes, which is closely related to that of the coagulation of colloid suspensions, is one of much interest.



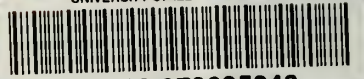








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